

## Supporting Information

# Electrocatalytic Detection of Ethanol and Acetaldehyde by Aminoxy Radicals: Utilizing Molecular Catalysis for Breath Analysis

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### Experimental Section

#### General Details

All solvents and chemicals were attained from commercial suppliers and used without any purification. Voltammetric and chronoamperometric experiments were conducted using DropSens multichannel potentiostat/galvanostat. For homogeneous studies in aqueous phase, a 10 mL Pine electrochemical cell equipped with an Ag/AgCl (internal solution 3 M KCl) reference electrode, a Pt wire counter electrode, and a glassy carbon disk (2 mm) as the working electrode was used. For electrochemical studies in gas phase and some of the electrochemical studies in aqueous phase, screen-printed electrodes (SPEs) from DropSens were utilized. The SPEs that were used in these studies were fabricated with a Ag/AgCl ink as pseudo-reference electrode, and carbon ink as working and counter electrodes. The working electrodes had a 3 mm diameter. The electrode has three individual connections that can be inserted into an adapter connected to the potentiostat.

## Homogeneous Catalyst Studies

For the homogeneous studies in solution phase, a 10.0 mM stock solution of 4-hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxyl benzoate (TMB) was prepared by dissolving TMB (0.0276 g, 0.100 mmol) in 10 mL acetonitrile (MeCN). A 10 mL solution was prepared in the electrochemical cell by mixing 1 mL TMB stock solution, 2 mL MeCN, and 7 mL stock solution of supporting electrolyte and/or base and analyzed by cyclic voltammetry (CV) or chronoamperometry (CA).

The stock solutions of supporting electrolyte and/or base are:

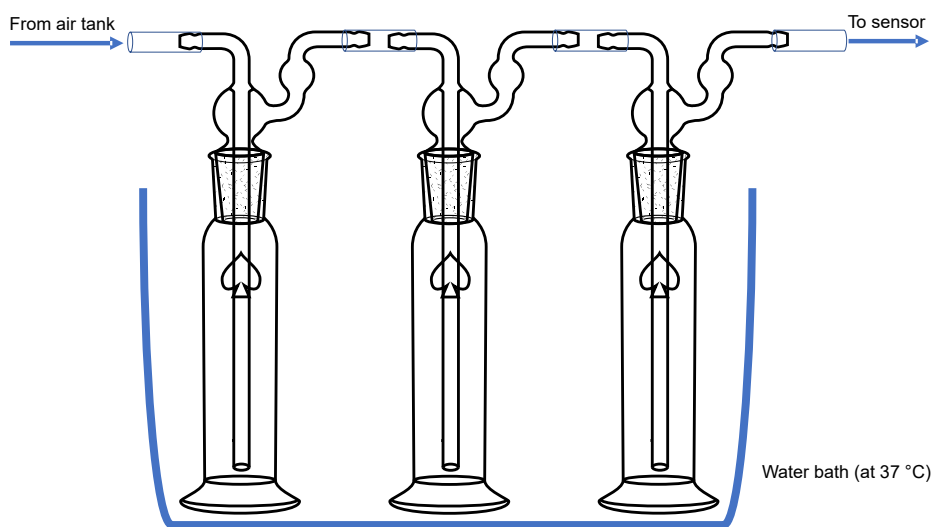
- 0.20 M NaCl was made by dissolution of 5.8 g NaCl in 500 mL D.I. water
- 0.20 M sodium acetate (NaOAc) made by dissolution of 8.2 g anhydrous NaOAc in 500 mL D.I. water
- 0.20 M 500 mL sodium bicarbonate (NaHCO<sub>3</sub>) by dissolution of 8.4 g NaHCO<sub>3</sub> in 500 mL D.I. water
- 0.20 M sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) by dissolution of 10.6 g Na<sub>2</sub>CO<sub>3</sub> in 500 mL D.I. water
- 0.20 M NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> buffer (0.1 M each) by mixing 1:1 stock NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>.

Voltammetric analysis at various scan rates was used for initial potential screening. For the chronoamperometry experiment the potential was adjusting at 100 – 150 mV more positive to the oxidation peak potential of the catalyst (determined from CV experiment) for the desired amount of time, typically 5 to 20 seconds. The desired amount of ethanol was added to the TMB-only solution in the electrochemical cell, following examination of the catalyst itself, to ensure the most accurate comparison between the cyclic voltammograms or chronoamperograms before and after its addition. For example, 12  $\mu$ L for a 20 mM solution was added using a 10-100  $\mu$ L micropipette.

## Generation of Simulated Breath with Ethanol/Acetaldehyde Content

For generation of a mixture of ethanol, air, and water similar to the breath, the setup in Figure S1 was used, in which the gas washing bottles were filled with water or aqueous solutions

of ethanol. 0.02%, 0.04%, 0.08%, and 0.16% (volume percent) solutions of ethanol were made by dissolution of 0.10, 0.20, 0.40 and 0.80 mL EtOH in 500 mL D.I. water. Considering the breath alcohol content (BrAC) to blood alcohol content (BAC) ratio of 1/2000 at human body temperature, the above-mentioned concentrations give the simulated breath corresponding to BAC.<sup>1</sup> A gas tank was used for bubbling air through the gas washing bottles, described in next section. BAC value of 0.080% is the federal limit to legally drive in the United States. For generation of a gas phase acetaldehyde, similar to the ethanol in breath, the setup in Figure S1 was used, in which the gas washing bottles were filled with water or aqueous solutions of acetaldehyde. With higher volatility of acetaldehyde, the breath to blood acetaldehyde ratio is 1/109. 0.001%, 0.002%, 0.004%, and 0.008% (volume percent) solutions of acetaldehyde were made by dissolution of 5, 10, 20, and 40  $\mu\text{L}$  of acetaldehyde in 500 mL D.I. water. To obtain the most accurate comparison of cyclic voltammograms and chronoamperograms before and after exposure to EtOH, the SPEs were first exposed to only water vapor for about 15 seconds. All solutions were maintained at 37°C while testing the SPEs using a warm water bath. Schematic presentation of the setup and its picture are shown in Figure S1 and the setup is shown S2.



**Figure S1.** Schematic presentation of the setup for generation of simulated breath.



**Figure S2.** Setup for gas phase studies using SPEs, including potentiostat with SPE connection, computer with DropSens software, nitrogen gas tank, and water bath containing gas washing bottles.

### **Carbon Paste Modified Screen-Printed Electrodes**

To fabricate the carbon paste, a specified amount of TMB was ground to a fine powder using a mortar and pestle. The desired carbon materials (listed below) were mixed with the TMB powder and paraffin oil was added until the proper paste consistency was obtained. TMB loading varied from 1, 2.5, and 5 mg in the paste. The optimized amount of paraffin oil and carbon-based materials are listed below.

- 0.2000 g graphene (G) and 0.2600 g paraffin oil with 0.0050 g TMB
- 0.1750 g G, 0.2600 g paraffin oil, and 0.0250 g NaHCO<sub>3</sub> with 0.0050 g TMB
- 0.0600 g decarboxylated graphene oxide (DGO) and 0.0460 g paraffin oil with 0.0025 g TMB
- 0.0600 g basic graphene oxide (BGO) and 0.0460 g paraffin oil with 0.0025 g TMB.

The amount of paraffin oil was adjusted slightly when adding different amounts of TMB or when adding solid or liquid bases to the paste. The carbon pastes were placed on the working electrode of a SPE for gas phase studies.

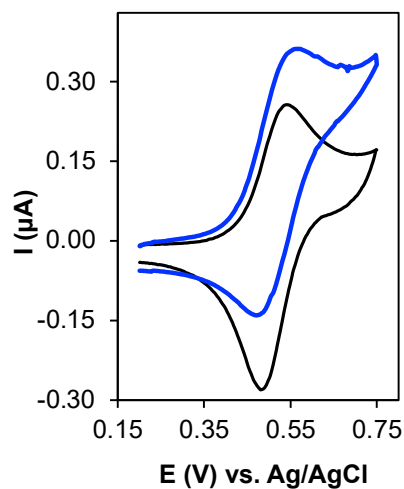
To make decarboxylated graphene oxide (DGO) for the carbon pastes, graphene oxide (GO) was treated with NaOH. Based on the reported value for oxygenated functional groups on GO (~11%), and about 3 mmol carboxylic acid functional groups per gram. Thus, the carboxylic acid groups in a 1 g sample of GO can be deprotonated by about 3 mmol of NaOH. A 1.0 M solution of NaOH was first prepared by dissolution of 0.4024 g NaOH in 10 mL D.I. water. GO (0.300 g) was added to 1 mL of 1 M NaOH in a small vial and the mixture was stirred for 30 minutes. After stirring, the vial was transferred to an oven under vacuum to completely dry the DGO. To prepare the basic graphene oxide (BGO), the same preparation was utilized, however the GO was treated with 2.5 times NaOH. It should be noted that more fine particles with lower charging current for DGO and BGO were obtained when they were allowed to dry rather than being isolated via vacuum filtration after treatment.

The surface of SPE working electrodes were covered with a layer of paste using a plastic strip that has a hole exactly the size of the working electrode and 0.5 mm thickness. For the aqueous phase study, the modified electrodes were immersed in a solution, or a droplet of solution was used to cover the surface of the electrode assembly. For the gas phase study, after modification of the SPE working electrode with the desired paste, the rest of the electrode assembly was covered with a layer of an ionic liquid, i.e., 1-Butyl-3-methylimidazolium tetrafluoroborate (BMIMBF<sub>4</sub>), in order to provide the ionic connectivity between the assembly of electrodes, making SPEs suitable for gas phase reactions. The electrodes were exposed to resulted gas from the setup as demonstrated in Figure S2.

### **Attempts on Optimization of Paste Composition**

Preliminary tests probed the redox activity of TMB on a carbon paste electrode fabricated by mixing graphene powder with paraffin oil or a variety of ionic liquids as binders.<sup>2,3,4</sup> TMB showed irreversible cyclic voltammetry features with no catalytic activity in ionic liquid-based carbon pastes, possibly due to the strong interaction between TMB<sup>+</sup>, as the reactive form of the

catalyst, with the anion of the ionic liquid, especially ionic liquids with basic anions.<sup>5</sup> Using paraffin oil as binder for the paste led to a reversible redox feature. Moderate catalytic activity was observed by incorporating both TMB catalyst and organic bases like carboxylate or pyridine derivatives into the composition of carbon paste electrode. However, incorporating TMB catalyst and bases like sodium bicarbonate has shown no catalytic activity, most likely due to the insolubility of inorganic bases in paraffin oil.



**Figure S3.** CVs of SPEs modified with carbon pastes made of paraffin oil, TMB, graphene and sodium benzoate. Black trace is in the absence and blue trace is in the presence of ethanol in the gas phase, scan rate  $25 \text{ mV s}^{-1}$ .

## References

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