Supplemental Info

Methods:

Electrochemistry. Fast-scan cyclic voltammograms were collected using a GeneClamp 500B potentiostat (Molecular Devices, Union City, CA) with a custom-modified headstage. Data was collected from a homebuilt data analysis system and two computer interface boards (National Instruments PCI 6052 and PCI 6711, Austin TX) were used to apply the waveform. The electrode was scanned from -0.4 V to 1.45 V (vs Ag/AgCl) and back with a scan rate of 400 V/s and a repetition rate of 10 Hz. Measurements were performed before and after modification with Nafion or Nafion-CNTs, so each electrode served as its own control. Electrodes were tested using flow-injection analysis as described previously.[34] Prior to data collection, electrodes were cycled with the waveform for 10 min in order to allow the background to stabilize.

Preparation of carbon-fiber microelectrodes. Cylinder electrodes, approximately 50 µm long, were used. Electrodes were epoxied with Epon Resin 828 (Miller-Stephenson, Danbury, CT) with 14% (w/w) 1,3-phenylenediamine hardener (Sigma-Aldrich, St. Louis, MO) to ensure a good seal. All electrodes were soaked for at least 10 min in isopropanol (Fisher Scientific) prior to use. Dip coating carbon-fiber microelectrodes with Nafion-CNT was chosen over electropolymerization due to the application voltage causing CNTs to aggregate and fall out of solution more quickly.

Functionalization of CNTs. 25-30 mg of CNTs were suspended in 100 mL of piranha solution (3:1 sulfuric acid: 30% hydrogen peroxide) and placed in a water bath sonicator for 24 hours at 0^{o}C. After approximately 19 hours, 5 mL of 30% hydrogen peroxide was added to the mixture to make up for hydrogen peroxide decomposition. After 24 hours, the CNT solution was “polished” by heating to 70^{o}C for 15 minutes. The CNT solution was diluted with 1 L of deionized water and vacuum filtered with a 0.22 µm filter paper and allowed to dry overnight. (Millipore, Ireland).

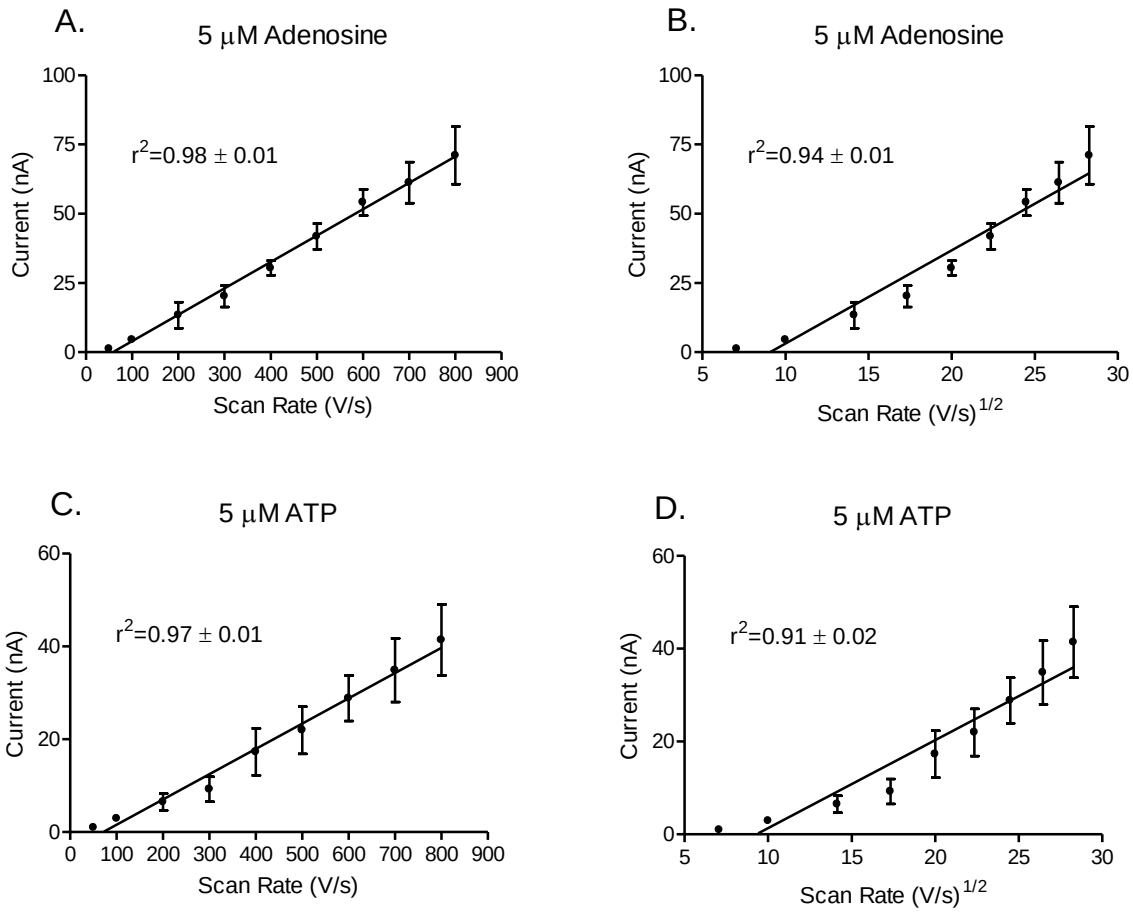

Figure S1: The electrochemical reactions observed after Nafion-CNT coated are primarily adsorption controlled. 5 μM adenosine and ATP were tested at Nafion-CNT electrodes for scan rates ranging from 50 V/s to 800 V/s. Plotting current versus scan rate and square root of scan rate shows if reaction is primarily adsorption or diffusion controlled. A and B) For adenosine, the electrochemical reaction at a coated electrode is primarily adsorption controlled because the current versus scan rate plot is more linear. C and D) For ATP, the electrochemical reaction is also primarily adsorption controlled at coated electrodes. (n=3).

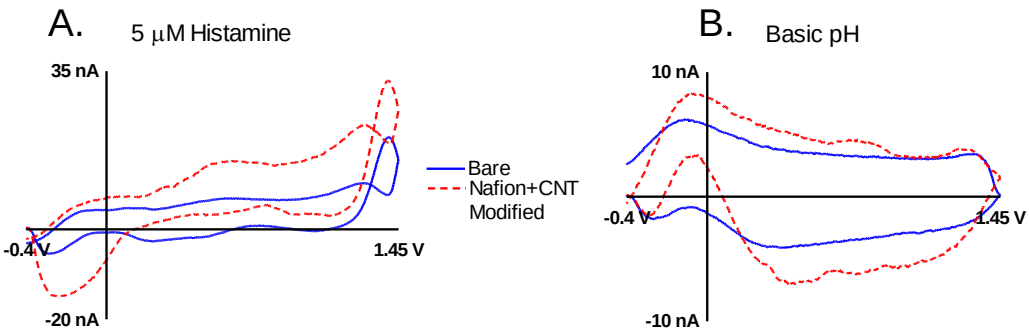

Figure S2: Cyclic voltammograms of A.) 5 μM histamine and B.) Basic pH shift of +0.2 pH units before and after Nafion-CNT coating. A 2-fold increase is seen for histamine and no change is observed for the basic pH shift.

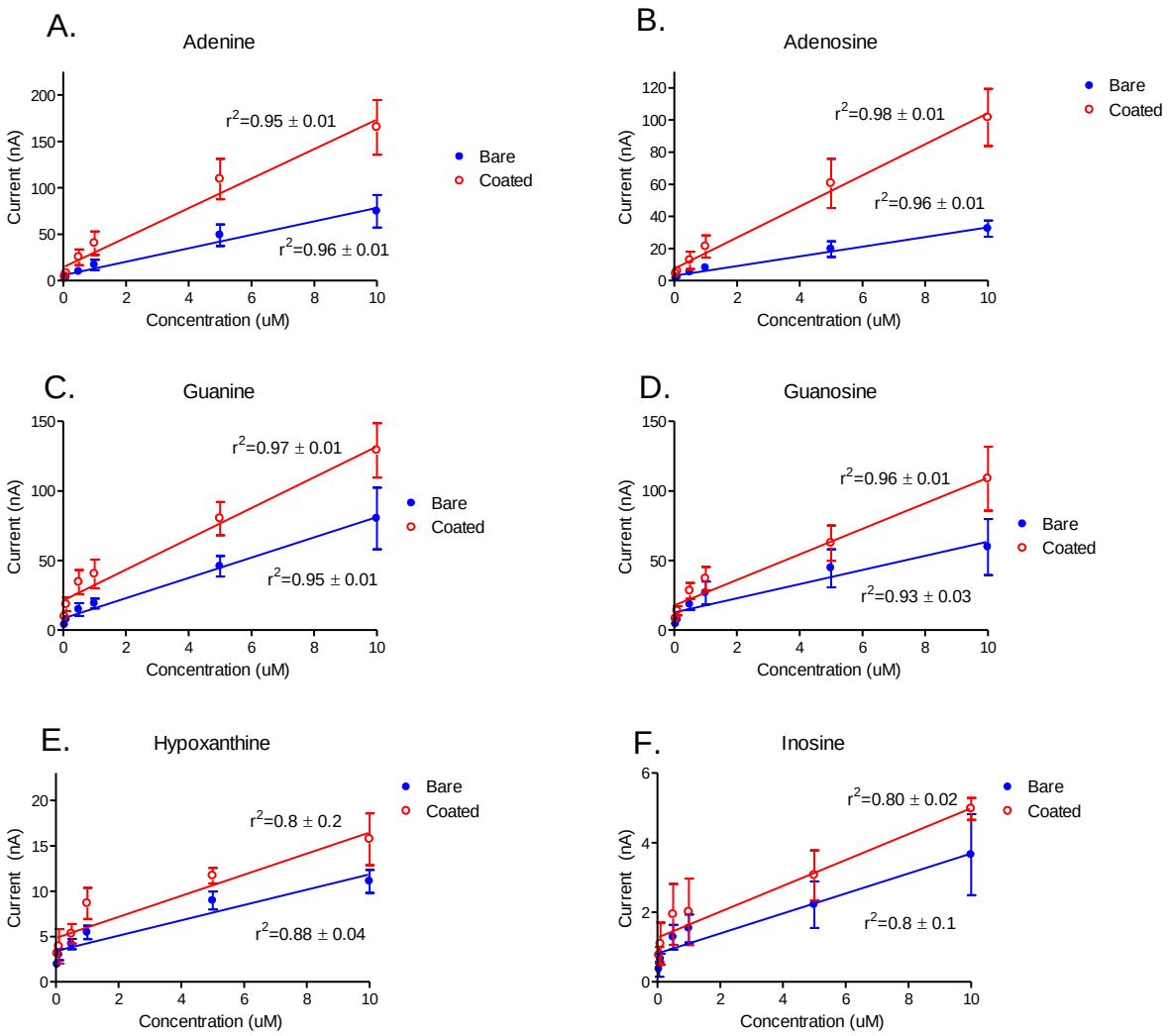

Figure S3: Calibration curves for purines and associate nucleosides for both bare and coated electrodes. A) Adenine B) Adenosine C) Guanine D) Guanosine E) Hypoxanthine and F) Inosine (n = 4). Hypoxanthine and inosine were the least linear for both bare and coated electrodes because the electrodes were less sensitive to these analytes. Most analytes showed an improvement in linearity after coating (exception: hypoxanthine, inosine, and adenine).

Table S1. Average Calibration Slope Improvement for Purines and Nucleosides

Adenine	2.2 ± 0.2
Adenosine	3.2 ± 0.1
Guanine	1.5 ± 0.2
Guanosine	1.8 ± 0.3
Hypoxanthine	1.4 ± 0.3
Inosine	1.3 ± 0.2

Average data are the ratio of modified calibration slope to bare calibration slope for each analyte. Values given are ± SD for n = 4.