Electronic Supplementary Information
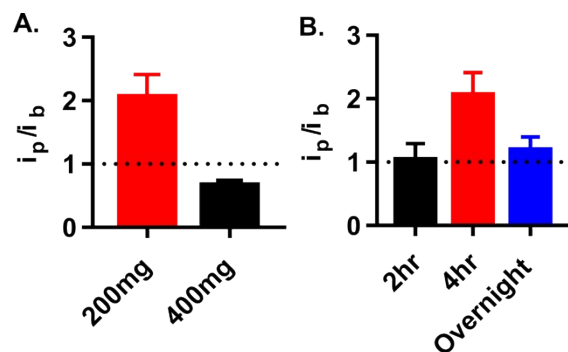
Amine-Functionalized Carbon-Fiber Microelectrodes for Enhanced ATP Detection with Fast-Scan Cyclic Voltammetry

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Figure S-1. The concentration of EDC and reaction time were optimized for maximal increase in oxidative ATP current. (A) The amount of EDC was compared between 200mg and 400mg in 2mL EDA at 4-hr reaction time. Larger amounts of EDC caused precipitation and agglomeration in solution which were detrimental to the electrode surface therefore, 200 mg was chosen as optimal (n = 4- 9). (B) A 4 hour reaction time is optimal for adequately functionalizing the surface with amines for improved ATP detection. The amount of EDC (200 mg) and EDA (2 mL) was held constant with varying the reaction time. All electrodes were electrochemically pretreatment prior to EDC/EDA modification (Electrochemical pretreatment waveform: -0.5 V to 1.8 V and back at 400 V/s for 5 min). Graph shows ratio of current post-test (i_p) to the unmodified/bare carbon fiber (i_b) for 5 µM ATP (n = 4-10). Ratios above 1.0 (dotted line) indicates an increase in oxidative current after treatment.
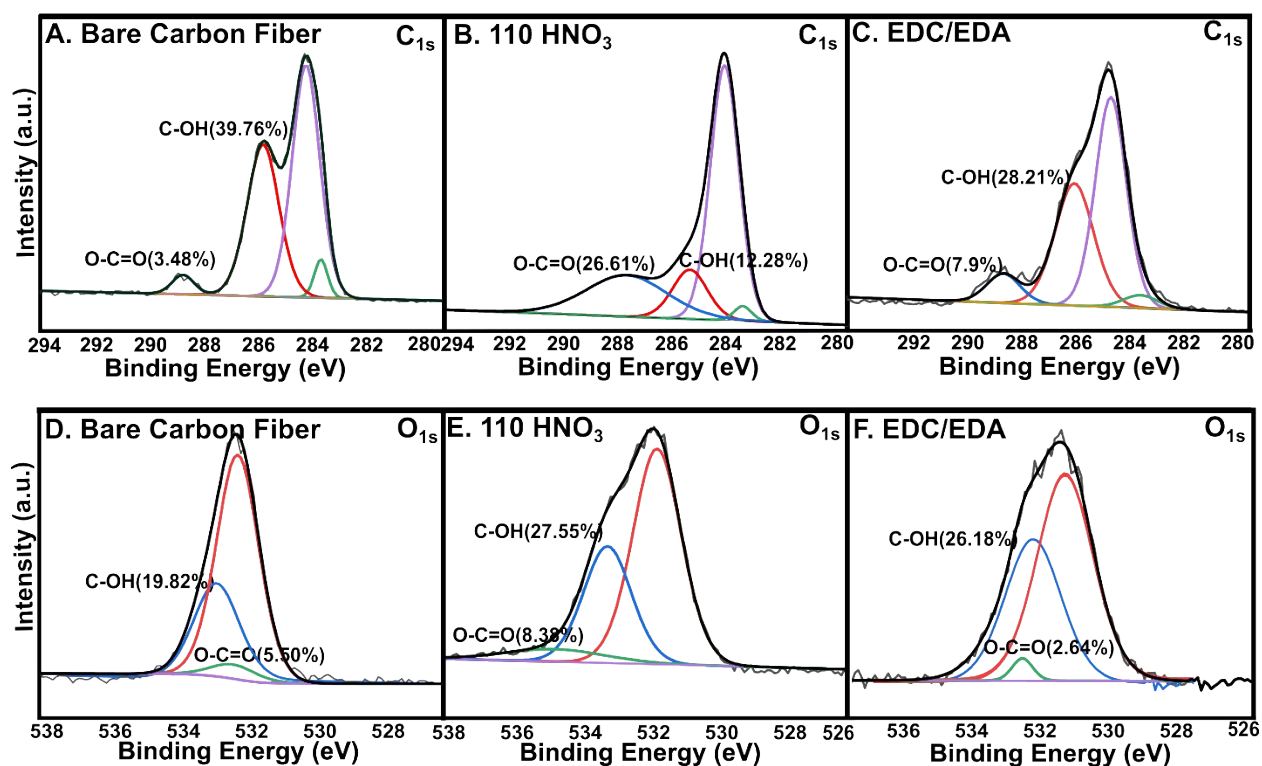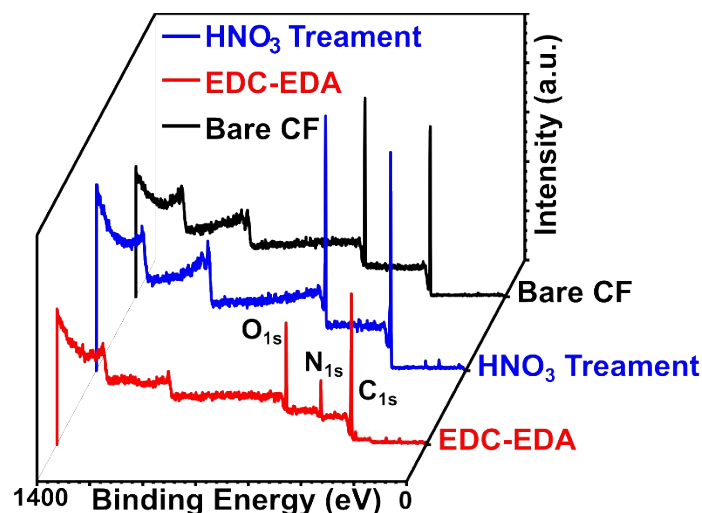
Figure S-2. Nitric acid treatment increases surface carboxyl groups while EDC/EDA treatment decreases carboxyl groups while increasing amine groups. Survey spectra is for bare carbon-fiber, fibers treated with 110 °C HNO3, and EDC/EDA modified carbon fibers. Analyzing the C1s and O1s peak for bare carbon fiber (A and D). (B) 27 % of the C1s peak for acid treated fibers is carboxyl groups and 12.3 % is hydroxyl groups. (C). After EDA/EDC, the carboxyl group functionality significantly decreases to 8%. Analyzing the O1s peak demonstrates the same findings (E and F).
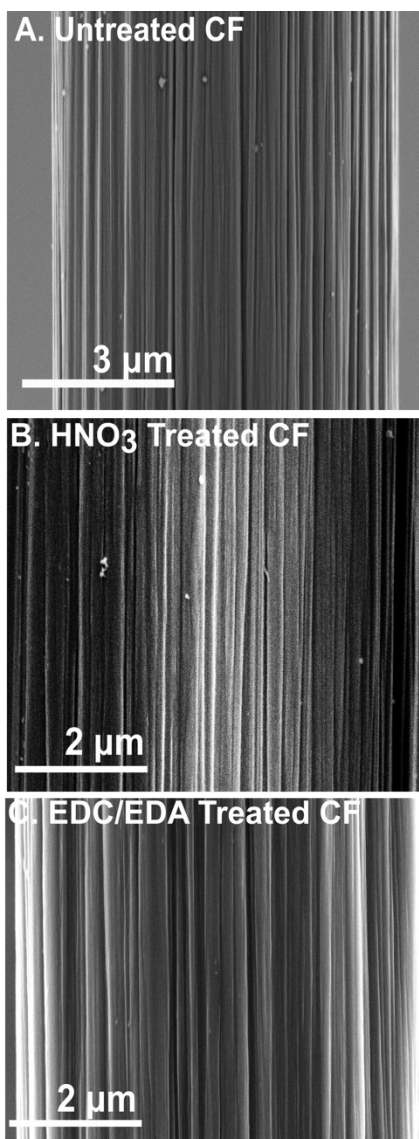
Figure S-3. Acid treatment for 30 min and EDC/EDA modification does not significantly change the topology of the carbon-fiber surface. Example SEM images for (A). Bare carbon fiber; (B). 110° C HNO$_3$ treated carbon fiber for 30 mins; (C). EDC/EDA treated carbon fiber. Scale bar is shown on each image.
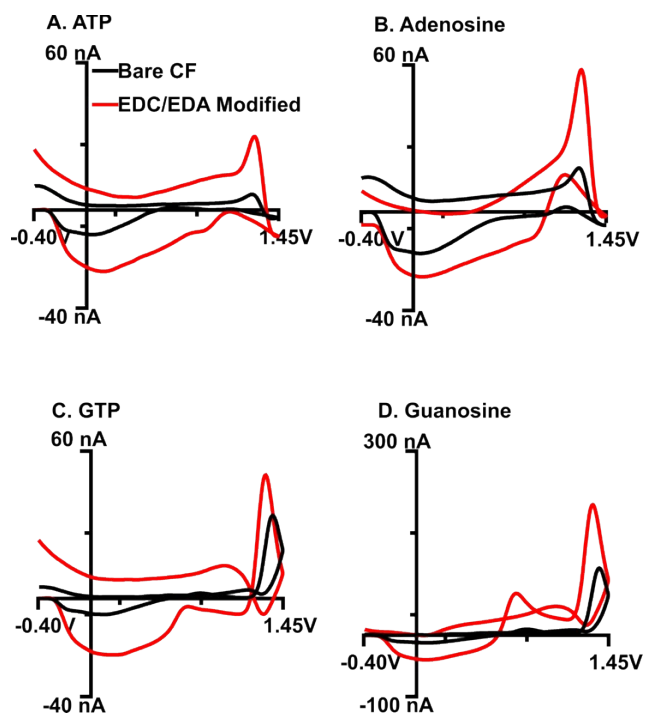
Figure S-4. NH$_2$-modified electrodes improve interaction of purines at the electrode surface potentially by facilitating hydrogen bonding at the surface. Example CV's are shown for before modification (black) and after EDC/EDA modification (red) for (A) 5 µM ATP; (B) 5 µM adenosine; (C) 5 µM GTP; and (D) 5 µM guanosine.

Table 1. ATP measurement techniques comparison

Sensor Type	LOD	Temporal resolution
ATP Aptamer-based sensors	2.5 to 24 µM[1,2]	Milliseconds to minutes[2]
Nanoaptamer sensor	45 pM to 61 µM[3,4]	Minutes[4,5]
MOF ATP Sensor	5.6 nM[6]	Seconds to minutes[7]
ATP Enzyme Sensor	40 nM[8]	Seconds to Minutes[8]
EDC/EDA modified CFME with FSCV (this work)	124 nM	Milliseconds to seconds

Supplemental References:
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