Supporting Information

Analysis of electrochemical properties of *S*-adenosyl-L-methionine and implications for its role in radical SAM enzymes

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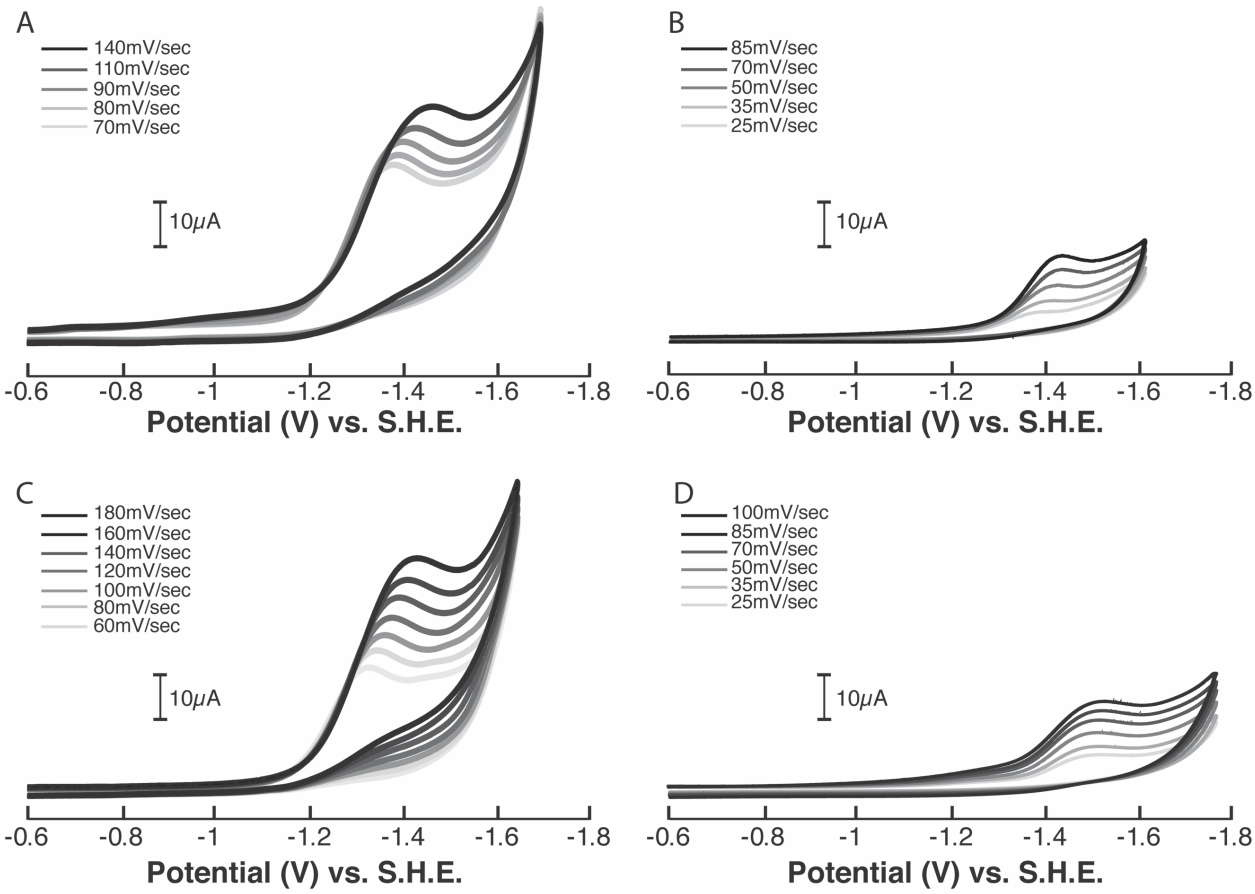

Figure S1. *Solvent and scan rate dependence of reductive wave and currents in CV experiments with SAM*. The reactions were carried out as described in the Experimental Procedures in (A) acetonitrile, (B) ethanol, (C) water, and (D) tetrahydrofuran. The peak currents are plotted in **Fig. S2**.

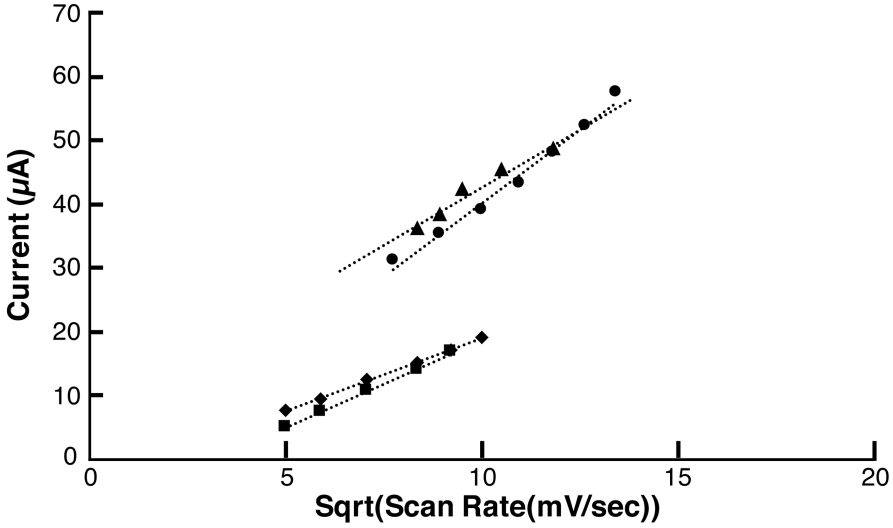

Figure S2. *Dependence of SAM reductive peak current on scan rate*. Plots of peak potentials from CV of SAM in various solvents form **Fig. S1**. The reactions were carried out in (circle) water, (square) ethanol, (triangle) acetonitrile, and (diamond) tetrahydrofuran.

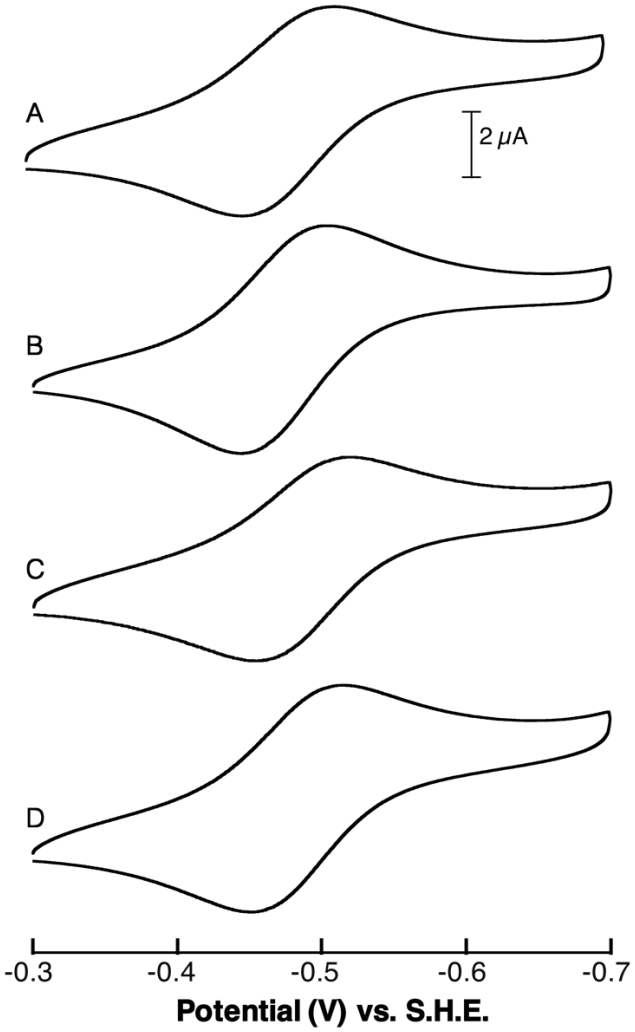

Figure S3. *Cyclic voltammograms of Methyl Viologen (MV).* All data was collected using a 0.1 mM MV, 0.2 M KCl solution with a scan rate of 100 mV/sec using a glassy carbon working electrode that had previously been utilized to determine scan rate dependence measurements with SAM (see **Figure S1**) in (A) water, (B) ethanol, (C) acetonitrile, and (D) tetrahydrofuran. Peak separation (ΔEp) and midpoint potential (E_o') vs. S.H.E. for MV are as follows; (A) ΔEp= 66 mV, E_o'= -438 mV (B) ΔEp= 66 mV, E_o'= -438 mV; (C) ΔEp= 64 mV, E_o'= -444 mV; (D) ΔEp= 64 mV, E_o'= -438 mV.

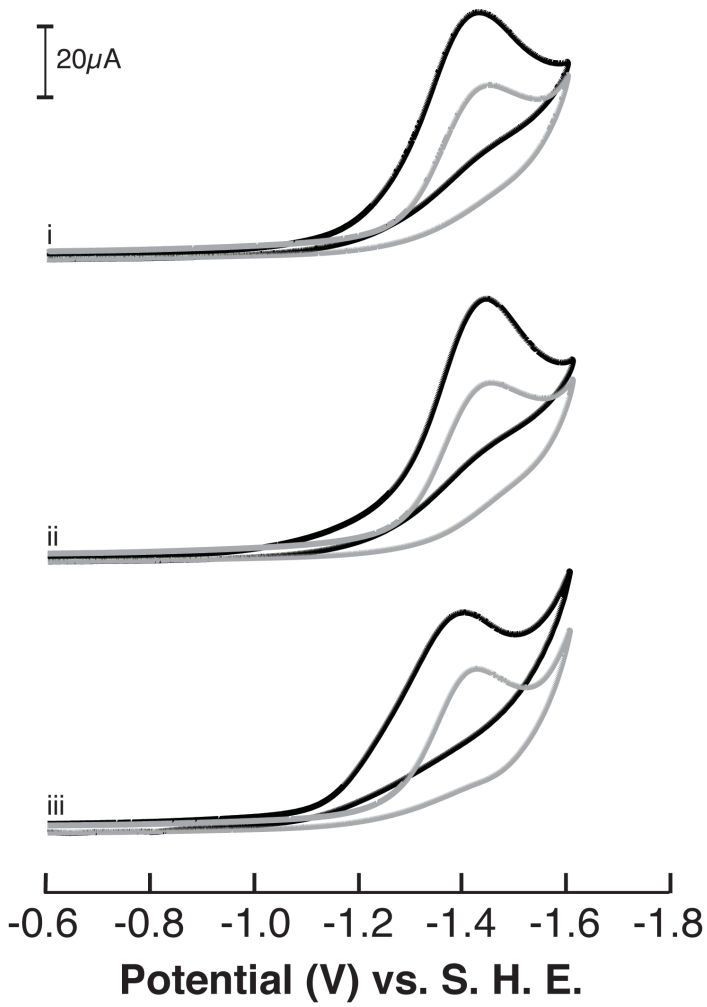

Figure S4. *Cyclic voltammetry of commercial (gray) and enzymatically prepared SAM (black) in* (i) 0.1 M KBr, (ii) 0.1 M KCl, and (iii) 0.1 M KI. All scans were collected at a scan rate of 140 mV/sec using a glassy carbon working electrode.

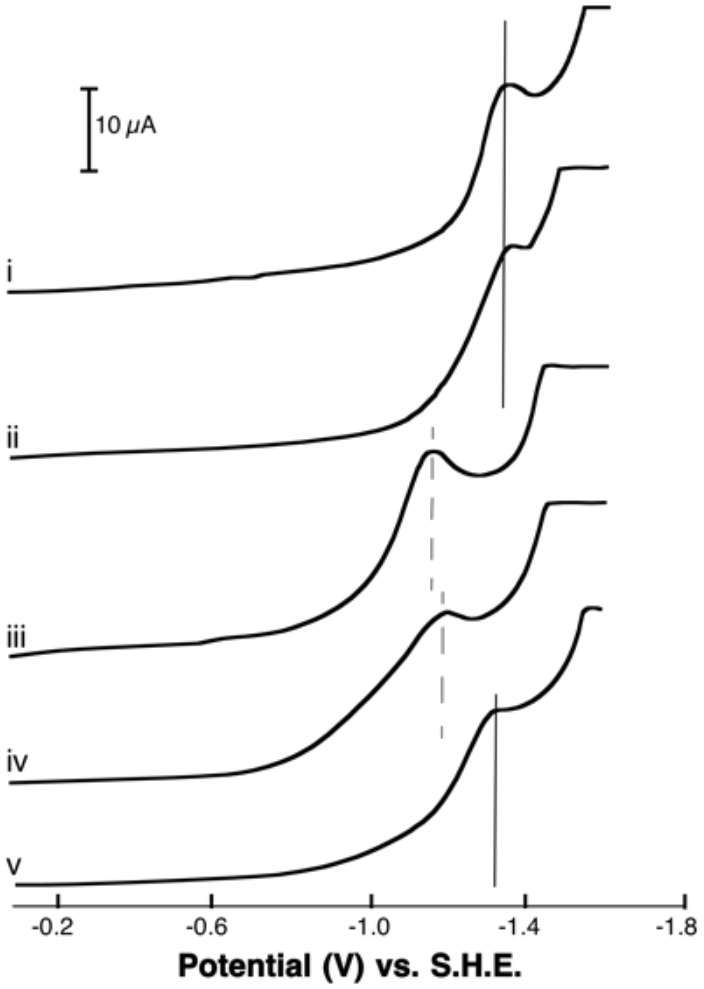

Figure S5. *Glassy-carbon working electrode functionalization*. Electrode functionalization was tested by obtaining CV data for 2 mM SAM in acetonitrile using iterative scans. i) is the first sweep after mixing SAM. At this point the sample was swept twice and ii) represents the third sweep. After these initial sweeps, a potential of -1.6 V was applied for 300 s and followed by a fourth sweep (iii). Following two more sweeps of the sample trace iv was obtained. Trace v) was obtained after two additional sweeps.

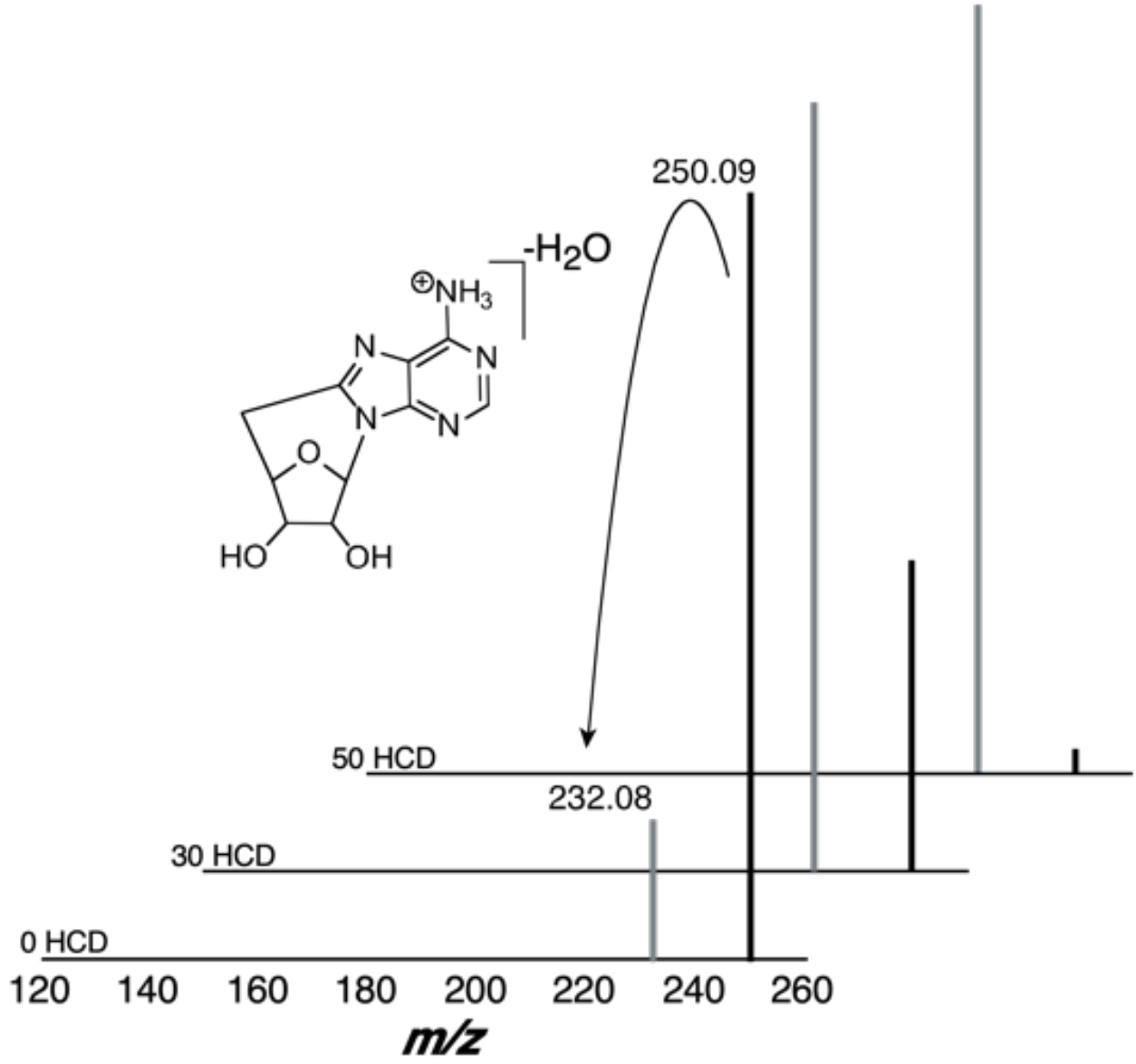

Figure S6. *Fragmentation of authentic cyc-dAdo standard in the HCD cell at various power settings*. The peak at *m/z* of 250.09 peak fragments to a species with *m/z* of 232.08 at increasing power.

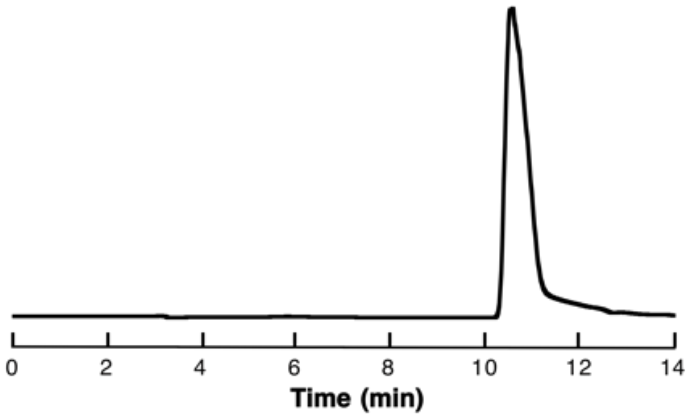

Figure S7. *EIC trace at m/z of 250 for a cyc-dAdo standard*. The separation was carried out as described in the Experimental Procedures.