Supporting Information

Electro-hydrogenation of nitrobenzene to phenylhydroxylamine with anthraquinone-2-sulfonic sodium as electron mediator

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Experiment section

Nitrobenzene and anthraquinone-2-sulfonic sodium are commercial products and are used without further purification. The reduction of NB to PHA is conducted in two separate areas: one for electrolysis and another for organic reaction. The solution of the electron mediator (0.1M AQSNa was dissolved by water with a water bath at 80℃) is placed in a cathode chamber and undergoes a constant current electro-reduction process (In an H-type cell: nafion117 proton exchange membrane, -0.025A/cm^2, 1M H_2SO_4 as anolyte; 0.1M AQSNa as catholyte, carbon plate as counter and reference electrode and carbon felt as working electrode, 3h with stirring only in cathode side) to get reduced mediator. Then, the reduced mediator reacts with NB (50 mM Nitrobenzene (MeCN: H_2O = 1:1 v: v) was prepared adding 510μL NB into a 100ml volumetric flask with 50ml MeCN and fill H_2O to volume) in the glass reactor under Ar atmosphere protection. The detailed procedures are: 1. Adding buffer solution/H_2O into the reactor; 2. Replace air with Ar; 3. Adding reactant and reduced $AQSH_2$ into the reactor; 4. Adding 1M Na_2SO_4 and H_2O, then using 1ml CH_2Cl_2 for extraction 3 times; 5. Using nylon 66 filter membrane to collect organic phase into 2ml vial for further characterization.

1M buffer solutions consist of different salts and their acid, Table S1 shows the components of buffer solutions at different pH values.

For further investigation of the reaction mechanism, we replaced the buffer solution with 1ml H_2O and measured the conversion and selectivity of NB/NSB reduction reactions without buffer solutions under identical conditions respectively.

Table S2 shows a very low reactivity of NB without buffer solution, while NSB shows a high conversion to PHA without buffer solution. This result indicates that the reduction of NB to NSB is the rate determination step of the NB reduction reaction, and NSB will quickly react with $AQSH_2$ to form PHA.

Product analysis and characterization

The analysis of the products from the reduction of nitrobenzene was performed by HPLC (making standard curves with PHA, NSB, NB, AN standard sample (MeCN: H_2O = 1:1 v: v), AOB, AB (Pure MeCN are used to dissolve AOB and AB), and undergoes the same process as normal reactions for example: adding same amount of buffer solution, reactant and H_2O, but replaced reduced $AQSH_2$ with AQSNa for a similar extraction conditions). Conditions: mobile phase A: H_2O, mobile phase C: Methanol, flow rate 0.8 cm^3/min. 0-20min Conc. C 40%; 20-40min Conc. C 65%; 40-50min Conc. C 40%. The conversion and Selectivity of reactions are calculated as follows formula:

$$Conversion\ (\%) = \frac{[NSB] + [PHA] + [AOB] * 2}{[NB] + [NSB] + [PHA] + [AOB] * 2} * 100\%$$

Taking PHA selectivity as an example:

$$PHA\ Selectivity\ (\%) = \frac{[PHA]}{[NB] + [NSB] + [PHA] + [AOB] * 2} * 100\%$$

The qualitative analysis of product PHA is performed by HPLC-MS and shown in Figure S1:

We did blank experiments with/without the electrochemistry: NB and NSB as reactants reacted with AQSNa (without electrochemistry)/$AQSH_2$ (with electrochemistry) (Figure S2) Reaction condition: Same with Fig. 2a.

We measured conversions of substituted nitrobenzene (Table S3). Due to the instability of substituted hydroxylamines, it is challenging to obtain their reference standards for quantitative analysis. Therefore, 1-methyl-3-nitrobenzene and 4-nitrophthalonitrile are selected for a scope of our off-field system. HPLC and ^{1}HNMR data of substituted nitrobenzene are shown in Figure S5-8.

Mechanism and reaction energy diagram

We carried out the CV analysis of AQSNa with and without NB at the selected pH. As the pH value increases, the ipa of AQSNa decreases, which indicates a stronger interaction between NB and mediator. (Figure S3)

We measured the apparent activation energy for the reduction of NB to PHA at 20, 30, 40, and 50 ^oC (without buffer solution to control these reactions at a lower conversion; NB/$AQSH_2$= 2.4; 400 rpm; 45 min). (Figure S4)

Table S1. Components of different buffer solutions

	HA	A^-
pH=2	H_3PO_4	KH_2PO_4
pH=3-6	HAc	NaAc

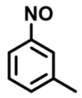
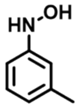
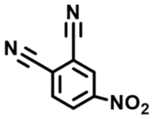
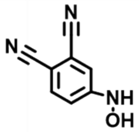
pH=7–8	KH_2PO_4	K_2HPO_4
pH=10–12	K_2HPO_4	K_3PO_4

Table S2. Conversion and Selectivity of NB/NSB reduction without buffer solutions

		HPLC analysis (% selectivity)			
Reactant	Conversion (%)	PHA	NSB	AOB	NB
NB	3.0	92.0	8.0	0.0	-
NSB	97.5	97.4	-	2.5	0.1

Reaction conditions: Ar atmosphere; $AQSH_2$/NB molar ratio=2.4; $AQSH_2$/NSB molar ratio=1.2; 1ml H_2O; 600rpm; 45min.

Table S3. The reduction of substituted nitrobenzene using $AQSH_2$ as electron mediator[a]

Sample	Substrate	Product	Substrate conv.[b] /%	Product Yield[b] /%
1			98.1	96.1
2			99.8	99.6

[a] Reaction conditions: AQSH$_2$/substrate molar ratio =3, 600rpm; 1.5h. [b] Calculated by ^{1}HNMR data.

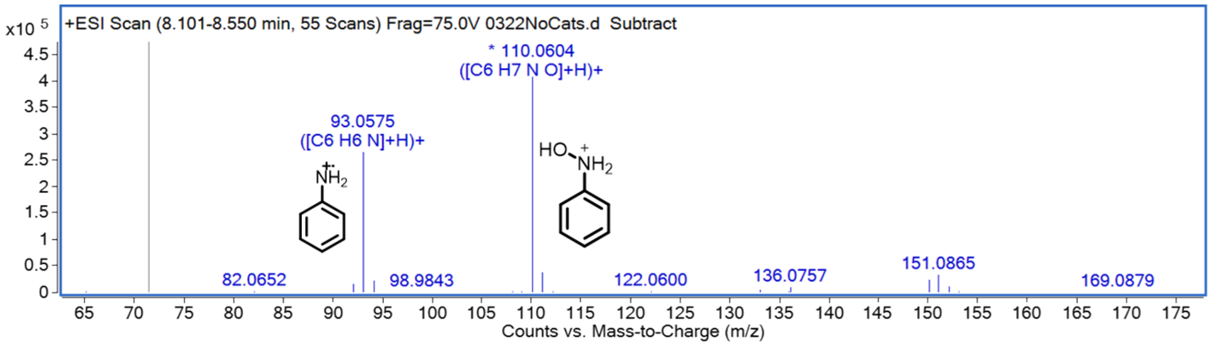


Figure S1. MS spectrum of the product PHA

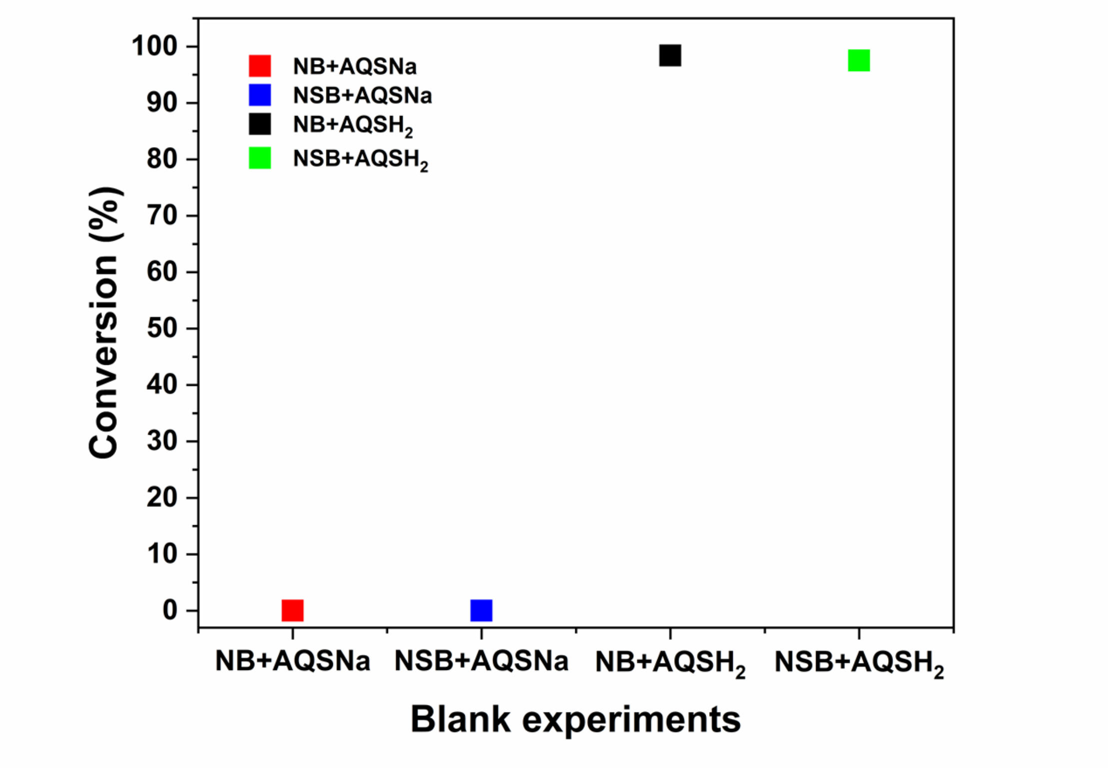


Figure S2. Blank experiments of NB/NSB reduction reactions (Reaction conditions: room temperature; 1 M HAc/NaAc buffer solution (pH = 4.8). $AQSH_2$ is replaced by AQSNa in the blank experiments.

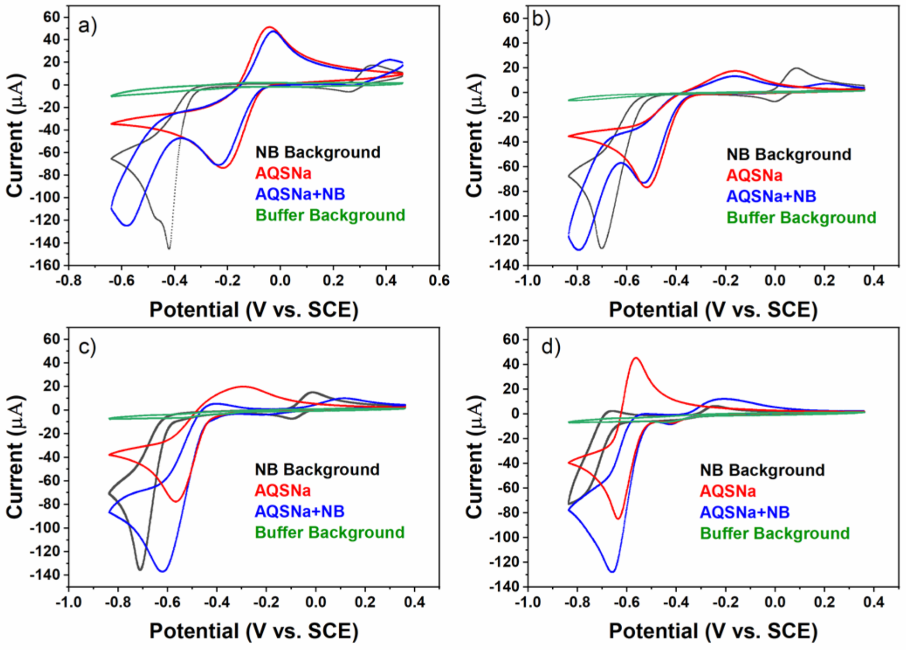


Figure S3. CV curves of AQSNa at different pH with/without NB. a) pH=0; b) pH=5; c) pH=7; d) pH=10. (concentration of AQSNa and NB is 10 mM, the concentration of different pH buffer is 100 mM; scan rate= 0.01 V/s) A glassy carbon electrode employed as the working electrode, a 2 * 2 cm^2 Pt plate serving as the counter electrode, and a saturated calomel electrode as the reference electrode

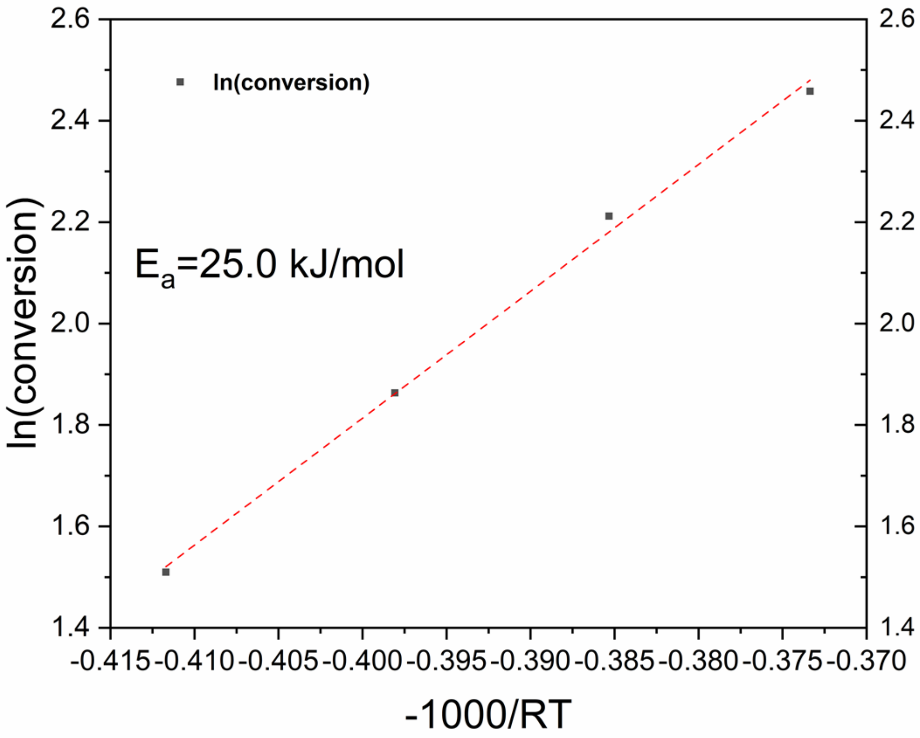


Figure S4. Apparent activation energy for the reduction of NB to PHA

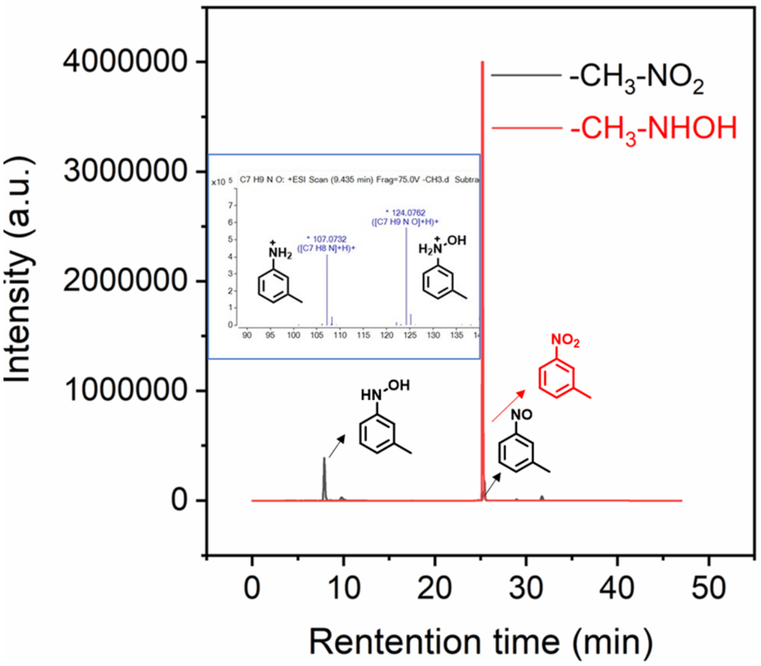


Figure S5. HPLC-MS spectrum of 1-methyl-3-nitrobenzene after reaction

N-(m-tolyl)hydroxylamine δ_H (700 MHz, CDCl$_3$; Me$_4$Si) 7.12 (t, J = 7.7 Hz, 1H), 6.70 – 6.84 (m, 3H), 2.31 (s, 3H).

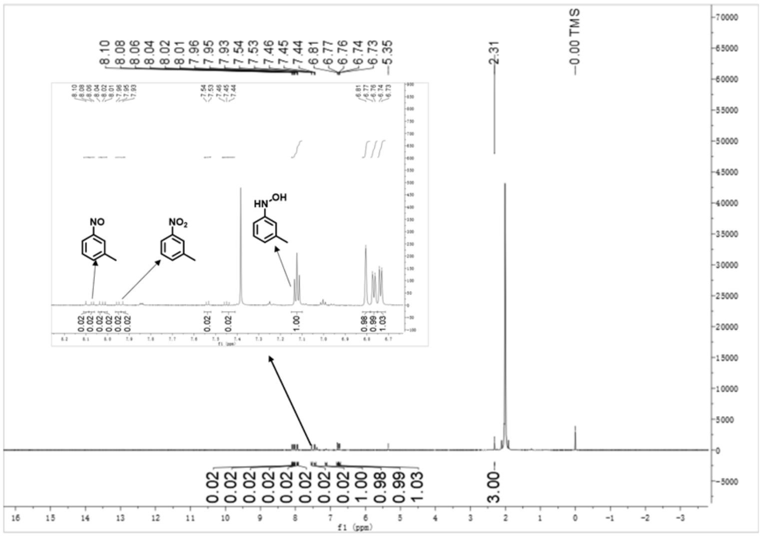


Figure S6. ^{1}HNMR result of 1-methyl-3-nitrobenzene after reaction (CDCl$_3$ with 1% (v:v) TMS 700MHz)

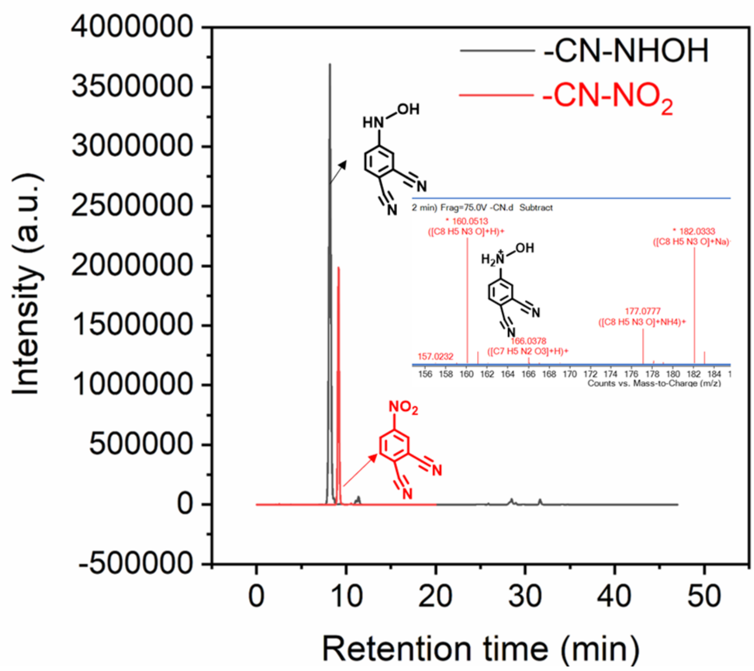


Figure S7. HPLC-MS spectrum of 4-nitrophthalonitrile after reaction

4-(hydroxyamino)phthalonitrile δ_H (700 MHz, $CDCl_3$; Me_4Si) 7.76 (s, 1H), 7.61 (d, J = 8.7 Hz, 1H), 7.29 (d, J = 2.2 Hz, 1H), 7.14 (dd, J = 8.7, 2.2 Hz, 1H).

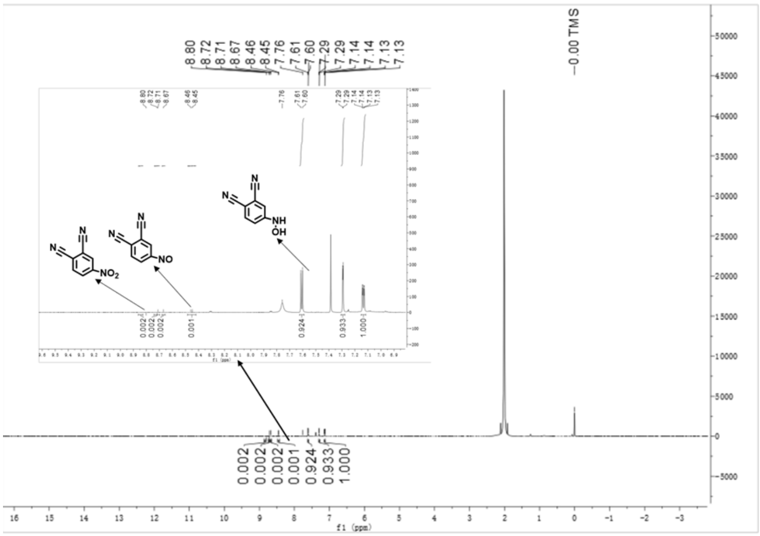


Figure S8. ^{1}HNMR result of 4-nitrophthalonitrile after reaction ($CDCl_3$ with 1% (v:v) TMS 700MHz)