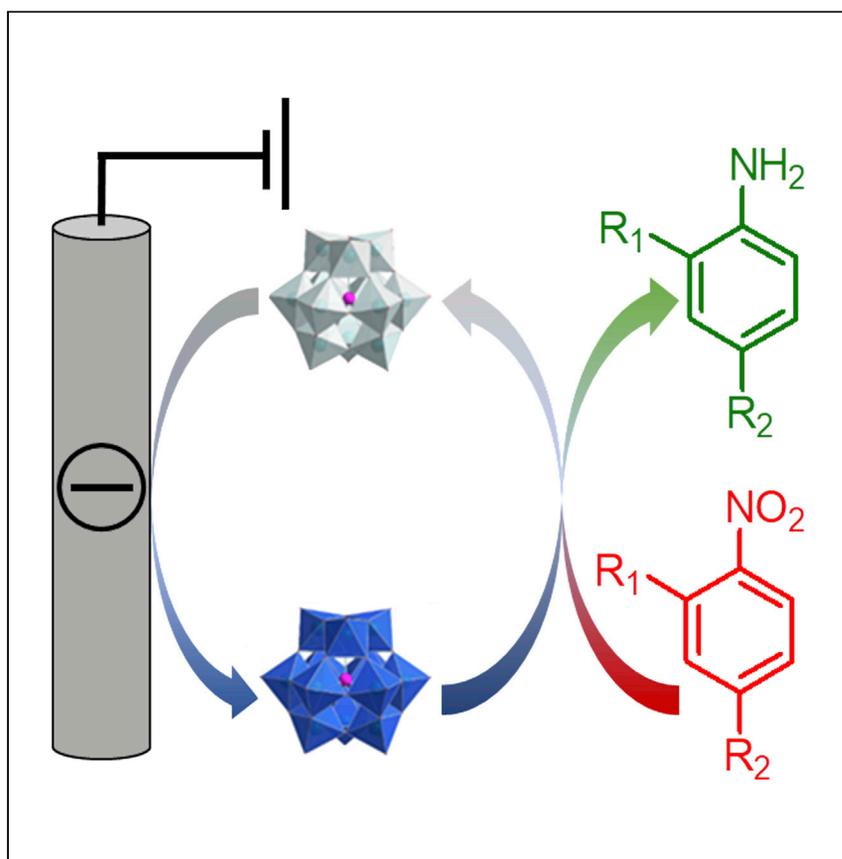


Article

# High yield and selective electrocatalytic reduction of nitroarenes to anilines using redox mediators



Anilines are major commodity chemicals that are usually produced via routes of questionable environmental sustainability. Stergiou and Symes report an electrocatalytic route to anilines that works in water at room temperature and pressure, holding promise for the development of more sustainable processes for the production of these vital chemical feedstocks.

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Highlights

Anilines are used extensively in the production of pharmaceuticals, dyes, and polymers

Current methods for the production of anilines are not environmentally sustainable

A more sustainable electrocatalytic redox-mediated route to anilines is reported

Reaction conditions are mild and selectivities for substituted anilines are high

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## Article

## High yield and selective electrocatalytic reduction of nitroarenes to anilines using redox mediators

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## SUMMARY

Anilines are major commodity chemicals used extensively in the production of pharmaceuticals, dyes, and polymers. However, the typical methods for synthesizing anilines suffer from poor environmental sustainability. Here, we report an electrocatalytic route for the production of anilines that works in aqueous solution at room temperature and pressure, where the electrons and protons required to reduce the nitrobenzene precursors are obtained from water. Excellent selectivities are obtained for a range of anilines, including species with ortho-iodides that are very challenging to obtain by other methods. Our approach relies on the use of a polyoxometalate redox mediator that shuts off the direct electro-reduction of the nitrobenzene at the electrode surface and thus prevents unproductive side reactions. Given the scale and current environmental impact of global aniline production, this electrochemical route holds promise for the development of more sustainable processes for the production of these vital chemical feedstocks.

## INTRODUCTION

Aromatic amines (anilines) are important building blocks in the synthesis of a wide range of nitrogen-containing compounds, including dyes, polymers, agrochemicals, and pharmaceuticals (e.g., one of the most widely produced pharmaceuticals, paracetamol, is a derivative of *p*-aminophenol).<sup>1–3</sup> Anilines are also the precursors for various important functional handles such as amides, diazonium salts, and imines, and thus access to a range of aniline derivatives is important for both industrial mass production of key commodity chemicals and also for the development of new synthetic methodologies and chemical discovery.<sup>1,4,5</sup> Currently, the most common way to produce these anilines is by the reduction of their corresponding nitro-compounds,<sup>6</sup> typically at temperatures of approximately 300°C and elevated pressure (5 bar). These methods also require the use of hydrogen gas and metal-based catalysts (Cu, Pd, Ni, or Pt) on activated carbon or oxidic supports, usually in combination with other metals (Pb, V, P, Cr, Fe) to enhance the selectivity.<sup>7</sup> Such catalytic systems are very effective for the reduction of unfunctionalized nitrobenzene to aniline, but for functionalized nitro-compounds, the selectivity of hydrogenation is variable.<sup>7</sup> For example, halogen-substituted nitroarenes are especially challenging to convert to their aniline derivatives using conventional methods as there is a tendency for hydro-dehalogenation to occur, forming side products where the halogen has been lost.<sup>7–9</sup> This is particularly true for ortho-substituted iodo-nitroarenes, where selectivity in reduction is often very difficult to achieve.<sup>8,9</sup>

In recent years, this lack of selectivity in the hydrogenation of functionalized nitro-compounds using traditional methods has spawned a number of studies examining

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alternative protocols for nitrobenzene reduction.<sup>10–15</sup> A common focus of such research is the substitution of H<sub>2</sub> gas by a different hydrogenation agent and/or avoiding the use of high temperatures and pressures. One such route involves the use of soluble hydrogenation agents in the presence of metal catalysts, allowing the hydrogenation to proceed without the direct use of H<sub>2</sub> gas under less harsh reaction conditions.<sup>1,16–18</sup> However, a considerable drawback of such approaches is that these reducing agents, such as sodium borohydride, formate, and hydrazine,<sup>1,13–15,19,20</sup> are toxic and are also irreversibly consumed during the hydrogenation reaction. Methods based on such sacrificial reagents are therefore inherently unsustainable.

In contrast, electrochemical reduction offers the prospect of a more sustainable route to aniline production, where the protons and electrons required for nitrobenzene reduction are obtained from water, rather than from expensive and/or toxic reagents. To date, however, electrochemical methods for the hydrogenation of nitrobenzenes have lacked selectivity. In a seminal study in 1979, Marquez and Pletcher investigated the direct electrochemical reduction of nitrobenzene at a Cu electrode in a mixture of aqueous organic solvents, using sulfuric acid as the proton source. Direct electrochemical reduction led to a mixture of products with the main product, *p*-aminophenol, obtained in 75% yield under optimal conditions, with aniline and azoxybenzene found to be only minor constituents of the product mix.<sup>21</sup> Since then, a number of studies reporting the electrochemical reduction of nitrobenzenes to anilines have been reported, as summarized in Table 1. Among these existing studies, the highest overall conversion (98%) and selectivity (99%) for nitrobenzene reduction to aniline have been reported by the Zhang group, using either a cobalt phosphide (CoP) nanosheet cathode or a cathode composed of Ti-supported Co<sub>3</sub>S<sub>4-x</sub> nanosheets with sulfur (S) vacancies (Table 1, entries 1 and 2),<sup>22,23</sup> although H<sub>2</sub> evolution competes with nitroarene reduction in both cases. Further inspection of Table 1 demonstrates that for all of the entries, at least one key facet of reaction (conversion of nitrobenzene, process conditions, faradic efficiency, and/or selectivity for aniline) is suboptimal. A truly selective, efficient, and mild condition electrocatalytic process for the reduction of a wide range of nitrobenzenes to their aniline derivatives has therefore yet to be reported.

Here, we demonstrate for the first time just such a selective and mild electrocatalytic process for the reduction of various nitrobenzenes to their aniline derivatives. Our approach circumvents the direct reduction of the nitrobenzene starting material at the electrode (which we show is the primary cause of the lack of selectivity in previous electrochemical studies), and instead uses a soluble redox mediator as an electron and proton shuttle to allow the clean and selective reduction of the nitro group to an amine in the presence of other functional groups that remain intact (–I, –OH, –COCH<sub>3</sub>, –COOCH<sub>2</sub>CH<sub>3</sub>). Our process is conducted in an aqueous medium that provides both the protons and electrons required for nitrobenzene reduction, and the resulting anilines are readily isolated without the need for extensive purification directly from the reaction medium after adjusting the pH and extracting into an organic solvent. The fact that this procedure allows the hydrogenation of functionalized nitrobenzenes to their aniline derivatives without the need to use H<sub>2</sub> gas, high temperatures, elevated pressures, co-catalysts, or sacrificial reagents marks it out as a promising potential alternative for the more sustainable production of these key chemical feedstocks.

## RESULTS AND DISCUSSION

### Approach and substrate scope

A schematic illustrating the electrochemical redox mediator approach<sup>33–35</sup> to nitrobenzene reduction is shown in Figure 1. A suitable mediator should therefore be

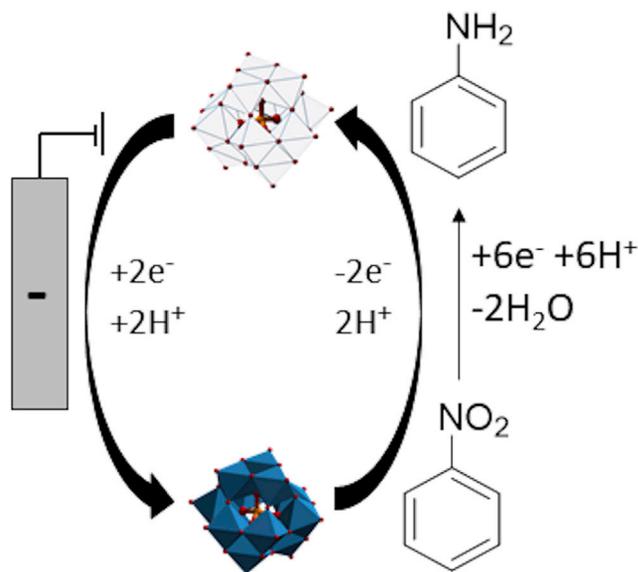
**Table 1. A summary of recent studies on the electrochemical reduction of nitrobenzenes to anilines**

Entry	Nitrobenzene conversion (%)	Aniline selectivity (%)	Other notable products	Process conditions	Reference
1	98	99	–	CoP nanosheet cathode (1 cm <sup>2</sup> ), –1.2 V versus Ag/AgCl, 1 M KOH	22
2	98	99	–	Ti-supported Co <sub>3</sub> S <sub>4-x</sub> nanosheets with sulfur vacancies (1 cm <sup>2</sup> ), –0.6 to –1.1 V versus Hg/HgO, 1 M KOH with traces (~4%) of CD <sub>3</sub> CN	23
3	61	87	nitrosobenzene (3.6%) <i>p</i> -ethoxyaniline (5.4%) azoxybenzene (3.3%)	N-containing ordered mesoporous carbon, –0.75 V versus Fc/Fc <sup>+</sup> , 52 h, 0.3 M HClO <sub>4</sub> ethanolic solution	24
4	44	<18	azoxybenzene (82%)	Cu/Cu <sub>x</sub> O MWCNT (multi-walled carbon), H <sub>2</sub> , –0.62 V versus Fc/Fc <sup>+</sup> , 52 h, 0.3 M HClO <sub>4</sub>	25
5	95	95	–	Carbon nanotube-modified packed-bed flow reactor, –1.20 V versus SCE in pH 5 solution, Faradaic efficiency 46%	26
6	51	8	azoxybenzene (77%)	Cu/Cu <sub>x</sub> O supported on Norit activated carbon, H <sub>2</sub> , –0.62 V versus Fc/Fc <sup>+</sup> , 52 h, 0.3 M HClO <sub>4</sub> ethanolic solution	27
7	not reported	87	–	Ti/TiO <sub>2</sub> electrodes, in 10% H <sub>2</sub> SO <sub>4</sub> , T = 50°C–60°C, cell potential 5–6 V	28
8	54	82	<i>p</i> -ethoxyaniline (11%)	Cu-PANI-AC-A, –0.75 V versus Fc/Fc <sup>+</sup> , 52 h, 0.3 M HClO <sub>4</sub> ethanolic solution	29
9	44	1	azoxybenzene (36%)	Cu/MWCNT (multi-walled carbon nanotubes), H <sub>2</sub> , –0.62 V versus Fc/Fc <sup>+</sup> , 52 h, 0.3 M HClO <sub>4</sub>	30
10	96.5	88.4	–	Nitrogen-doped diamond electrode, –0.9 V versus Ag/AgCl, 0.14 M Na <sub>2</sub> SO <sub>4</sub> , 26% Coulombic efficiency	31
11	5.3/pass	>99	–	Cu/C felt, –1 V cell potential, 5 wt % acetic acid in methanol/H <sub>2</sub> O (80:20 by weight)	32
12	>99	>99	–	Mediated process using as little as 1 mol % H <sub>3</sub> [PW <sub>12</sub> O <sub>40</sub> ] mediator; aniline is obtained in >90% isolated yield with up to 95% Faradaic efficiency	present study

AC, activated carbon; PANI, polyaniline

water soluble and exhibit excellent stability to repeated electrochemical cycling, with the ability to donate electrons to the nitroarene in a rapid and reversible fashion. Figure 2 shows that the polyoxometalate phosphotungstic acid (H<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>])<sup>36</sup> fits this specification well. As shown in Figure 2 (red line), phosphotungstic acid has two reversible (one-electron) redox waves located at –0.02 V and –0.30 V versus Ag/AgCl in 1 M aqueous H<sub>3</sub>PO<sub>4</sub> at pH 0.3. Upon the addition of 1 equiv of nitrobenzene to this phosphotungstic acid solution, there is evidence of an electrocatalytic process associated with the second reduction wave of phosphotungstic acid at –0.30 V versus Ag/AgCl (green line), indicating that the two-electron reduced phosphotungstic acid is reacting with nitrobenzene. Meanwhile, the direct reduction of an equivalent amount of nitrobenzene at the electrode surface in the absence of any mediator is shown by the blue trace in Figure 2; there is little appreciable activity for direct reduction at potentials more positive than –0.35 V versus Ag/AgCl. These data suggested to us that by careful control of the reaction conditions, it should be possible to reduce phosphotungstic acid by two electrons and have this two-electron reduced species react with nitrobenzene, without significant competing direct reduction of nitrobenzene at the electrode. In turn, we hypothesized that the outcome of this mediated process would be more selective than direct reduction of nitrobenzene at the electrode surface.

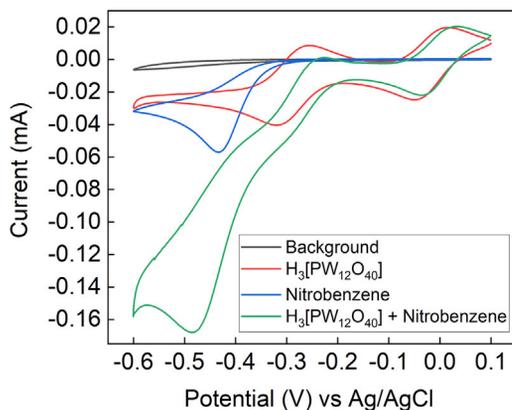
Accordingly, the catalytic electrochemical reduction of nitrobenzene to aniline was attempted. In a typical procedure, 0.1 equiv (10 mol %) of H<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] (concentration = 2.78 × 10<sup>–3</sup> M) relative to the nitrobenzene substrate was dissolved in the



**Figure 1. Schematic describing the electrochemical hydrogenation of nitrobenzene to aniline using a polyoxometalate redox mediator**

Phosphotungstic acid is electrochemically reduced at the surface of the electrode and then reacts with the nitrobenzene in solution to make aniline.

electrolyte solution and placed into one side (the “working electrode” side) of a two-compartment electrochemical cell (see [supplemental experimental procedures; Figure S1](#)). Meanwhile, the counter-electrode side was filled with 1 M aqueous  $\text{H}_3\text{PO}_4$ . The two chambers of the electrochemical cell were separated by a Nafion membrane to confine the starting materials and products to the cathode chamber as far as possible and to aid our determination of the reaction yields. Two large-area carbon felt electrodes were used as the anode and cathode, and an Ag/AgCl reference electrode was also used (except in those cases in which two-electrode operation was probed; see below). The relevant nitroarene substrate was added to the working electrode side of the cell, and this side of the cell was kept under an inert atmosphere of  $\text{N}_2$ . Electrolysis was then initiated (with constant stirring of the working electrode compartment) at  $-0.38$  V versus Ag/AgCl until substrate reduction was complete, as judged by the falling off of the current to background levels (see example in [Figure S2](#)). At the end of the reaction, the pH of the reaction medium was adjusted so that it was above the  $\text{p}K_a$  value of the anticipated product, and the reaction mixture was then extracted with an organic solvent. In the case of aniline, the pH value of the reaction mixture was raised to 6, using an aqueous 1 M NaOH solution, and chloroform was used for the extraction. Magnesium sulfate was then added to remove any remaining trace of water from the organic phase before concentration of this organic phase under reduced pressure. Other nitroarenes were isolated by similar methods (see [supplemental experimental procedures, SI-3.3](#) for details). The identity and purity of the various nitroarenes was then confirmed by NMR spectroscopy (see [supplemental experimental procedures; Figures S13-S30](#)). [Table 2](#) lists the yields and selectivity of conversion for a number of nitrobenzenes, showing excellent selectivity for the corresponding aniline derivatives over other possible products (indeed, typically only the aniline product was observed) and good-to-excellent yields. Cyclic voltammograms of these nitrobenzene starting materials can be found in the [supplemental experimental procedures \(Figures S6-S11\)](#). Conversion of the starting material was determined by  $^1\text{H}$  NMR analysis of the reaction



**Figure 2. Cyclic voltammetry showing the effects of phosphotungstic acid ( $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ ) on the reduction profile of nitrobenzene**

Cyclic voltammetry was performed in a single chamber cell, at a scan rate of 10 mV/s, using 1 M aqueous  $\text{H}_3\text{PO}_4$  (10 mL) as the electrolyte (pH 0.3) at 25°C. The working electrode was a glassy carbon button electrode (area = 0.071 cm<sup>2</sup>), a graphite rod was the counter electrode, and Ag/AgCl (3 M NaCl) was used as the reference electrode. The concentration of phosphotungstic acid was  $9.75 \times 10^{-3}$  M and 1 equiv (10  $\mu\text{L}$ ) of nitrobenzene was added to the electrolyte solution under inert atmosphere. The cyclic voltammogram of the 1 M aqueous  $\text{H}_3\text{PO}_4$  electrolyte on its own is shown as the black trace.

mixture after extraction into organic solvent (see [supplemental experimental procedures, SI-3.3 and SI-3.6](#) for details). [Figure 3](#) shows a stacked <sup>1</sup>H NMR plot summarizing the reaction outcome of the mediated reduction of nitrobenzene. Stacked <sup>1</sup>H NMR plots of the substrates and products of the other conversions are shown in [supplemental experimental procedures, SI-6](#). Reactions with a mediator can be compared to reactions in the absence of mediator, in which the nitrobenzene was undergoing direct reduction at the electrode surface (0% mediator loading entries in [Table 2](#)). In all of the cases without a mediator, yields of the aniline derivatives are substantially reduced. Direct reduction of nitrobenzene at the electrode ([Table 2](#), entry 1) proceeds with decent selectivity for aniline under these conditions (78%), although this is still significantly lower than that for the corresponding mediated process (>99% conversion). Apart from aniline, the main other species isolated from the reaction mixture of the direct reduction of nitrobenzene (in the absence of mediator) was azoxybenzene (13%, see [Table 3](#) and [Figures S13–S30](#)).

In the case of entries 2, 4, 5, and 6 in [Table 2](#), there is essentially no direct reduction of the nitrobenzene to the corresponding aniline (i.e., in the absence of mediator). For entries 4, 5, and 6, this is because there is only minimal conversion of the nitroarene starting material in the absence of the mediator. In the case of entry 2, conversion of the starting material in the absence of the mediator is quantitative, but the main product is the hydroxylamine intermediate (suggesting incomplete reduction) rather than the desired aniline derivative (see [supplemental experimental procedures, SI-6](#)). This is in stark contrast to the situation in which the polyoxometalate mediator is used, which gives essentially complete selectivity for nitroarene reduction to the corresponding aniline for all of the entries in [Table 2](#). Only in the case of *o*-iodonitrobenzene (entry 6) was a small amount (2%–6%) of the intermediate *N*-hydroxy-2-iodonitrobenzene identified. Isolated yields when using the mediator were generally good or excellent. In the case of aminophenol synthesis (entry 4), the comparatively low isolated yield (70%–75%) is a function of the very polar nature of this compound, which makes it difficult to separate the product from the aqueous reaction medium (see discussion in [supplemental experimental procedures, SI-3.3](#)). Meanwhile, the comparatively low isolated yields obtained for the

**Table 2. Obtained products with yields (relative to starting material) using 10 mol % loading of the mediator relative to the substrate**

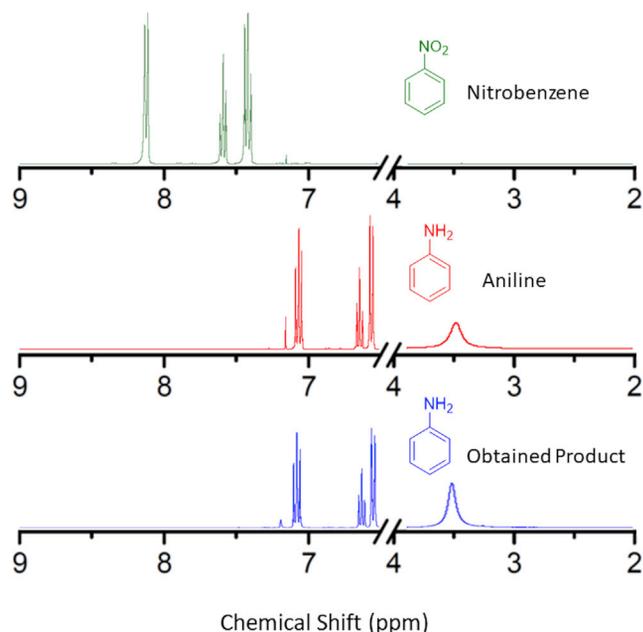
Entry	Substrate	Product	Using 10% mediator			Using 0% mediator		
			Conversion of starting material (%)	Selectivity for aniline (%)	Isolated yield of aniline product (%)	Conversion of starting material (%)	Selectivity for aniline (%)	Isolated yield of aniline product (%)
1			>99	>99	91 ± 2	95	78	60 ± 1
2			>99	>99	80 ± 3	>99	1.4 <sup>a</sup>	<1
3			>99	>99	81 ± 1	~77	~34	~25
4			>99	>99	72 ± 3	2.5	2.5	1
5			82 ± 2 <sup>b</sup>	>99	61 ± 4	0	0	0
6			97 ± 1	96 ± 2	71 ± 3	0	0	0

1 F = one equivalent of electrons. Reaction times for completion were between 5 and 12 h, as dictated by the relative solubility of the starting material.

<sup>a</sup>The main product of this reaction is the hydroxylamine intermediate, 2-hydroxylaminoacetophenone, as identified by <sup>1</sup>H NMR and mass spectrometry (see [supplemental experimental procedures](#)).

<sup>b</sup>After a reaction time of 12 h, approximately 18% starting material was still left unconverted.

two iodoaniline substrates (entries 5 and 6) are attributed to the lower solubility of these two compounds in the 1 M aqueous H<sub>3</sub>PO<sub>4</sub> electrolyte compared to the other starting materials that were used.



**Figure 3. Stacked <sup>1</sup>H NMR plot (CDCl<sub>3</sub>, 300 K, 400 MHz) summarizing the outcome of the mediated electroreduction of nitrobenzene**

Shown in green at the top is a spectrum of the nitrobenzene starting material. Beneath this (red) is a spectrum of a pure aniline standard sample. The bottom spectrum (blue) is that of the extracted and concentrated reaction medium from a mediated electrochemical reduction of nitrobenzene. The peak at 7.26 ppm originates from residual CHCl<sub>3</sub>.

### Probing reaction conditions

The reduction of unfunctionalized nitrobenzene to aniline was selected for in-depth investigations regarding catalyst loading and mechanistic studies. The effect of mediator loading on reaction times, average current densities, and product distributions was assessed, as shown in Table 3. These results show that the selectivity toward aniline remains at >99% when using 1 mol % loading of the mediator (entry 2), with isolated yields (~90%) and Faradaic efficiency (94%) essentially indistinguishable from that obtained using 10 mol % loading. At 0.1 mol % mediator loading (entry 3), side products are evident and the yield of aniline is reduced, and this trend is even more pronounced in the absence of mediator (where only direct reduction of the nitrobenzene at the electrode surface is occurring [entry 4]). It therefore seems likely that at very low mediator loadings, some direct reduction of the nitrobenzene is happening at the electrode surface, leading to side product formation (see mechanistic discussion below). That said, even at 0.1 mol % mediator loading, conversion of nitrobenzene to aniline is significantly cleaner and side-product formation correspondingly lower than for the direct process.

The reduction of nitrobenzene to aniline is also effective under air (Table 3, entry 5). In this case, there was still >99% selectivity toward aniline (isolated yield of 91%), but the Faradaic efficiency declined to 73% (compared to 95% under inert atmosphere). One reason for this is surely that the two-electron reduced mediator can be re-oxidized by oxygen in the air, and so some charge is lost to this aerial re-oxidation, rather than going toward nitrobenzene reduction (see supplemental experimental procedures, SI-3.5 and Figure S3 for details of the aerial re-oxidation of the mediator under these conditions). It is striking, however, that the introduction of oxygen has no more serious effect on the reaction outcome than this moderate loss in efficiency,

**Table 3. Summary of the effects of different mediator loadings on the electrochemical reduction of nitrobenzene, including yields (relative to starting material), the selectivity toward different products (as gauged by <sup>1</sup>H NMR), Faradaic efficiencies, and reaction times**

Entry	Mediator loading (%)	Time (h)	Average current density (mA/cm <sup>2</sup> ) <sup>a</sup>	Nitrobenzene conversion (%)	Aniline selectivity (%)	Azoxybenzene selectivity (%)	Phenylhydroxylamine selectivity (%)	Nitrosobenzene selectivity (%)	Isolated yield of aniline (%)	Faradaic efficiency (%)
1	10	5	-5.31	>99	>99	0	0	0	89–93	95
2	1	18	-2.58	>99	>99	0	0	0	89–92	94
3	0.1	23	-1.75	98	94	1.4	2	0.6	83–85	93
4	0	24	-1.97	95	78	13	2	2	59–61	89
5	10 <sup>b</sup>	16	-5.26	>99	>99	0	0	0	91	73
6	10 <sup>c</sup>	23	-0.14	15	>99	0	0	0	13.8	94
7	0 <sup>c</sup>	20	-5.93 × 10 <sup>-3</sup>	0	0	0	0	0	0	0
8	10 <sup>d</sup>	14	-4.11	>99	>99	0	0	0	90	94
9	0 <sup>d</sup>	22	-0.28	24	9.9	9.4	4.7	0	7	25
10	10 <sup>e</sup>	40	-3.4	>99	>99	0	0	0	82	83
11	10 <sup>f</sup>	15	-2.21	>99	>99	0	0	0	91	90

<sup>a</sup>Over the first 2.5 h of the reaction.

<sup>b</sup>Reaction performed under air.

<sup>c</sup>Reaction performed at a potential of -0.2 V versus Ag/AgCl.

<sup>d</sup>Reaction performed at a potential of -0.3 V versus Ag/AgCl, with Pt mesh as the counter electrode.

<sup>e</sup>1.23 g nitrobenzene (10 mmol) was used for scaling-up purposes.

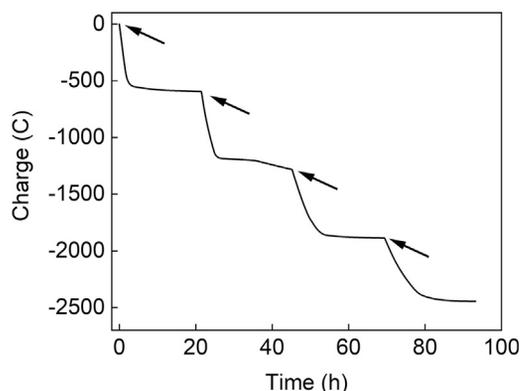
<sup>f</sup>Two-electrode setup with cell voltage of -2.2 V and using Pt mesh as the counter electrode.

and aniline is still the only reduction product obtained when the mediator is used under air.

Entries 6 and 7 in Table 3 compare the conversion and selectivity for nitrobenzene reduction at an applied potential of -0.2 V versus Ag/AgCl. As shown in Figure 2 and entry 7 in Table 3, this potential is clearly not cathodic enough to allow the direct electroreduction of nitrobenzene to aniline at the electrode. However, entry 6 shows that there is a 15% conversion of nitrobenzene to aniline at this potential in the presence of the mediator. This is strong evidence that the mediated pathway occurs at lower potentials than the direct pathway, in turn suggesting a route by which the greater selectivity of the mediated pathway is achieved. As the potential is made more cathodic (-0.3 V, entries 8 and 9), the direct electroreduction reaction becomes possible, but the mediated pathway shows considerably greater current density and also far superior selectivity for aniline.

The final two entries in Table 3 suggest that the mediated route from nitrobenzene to aniline shows some promise for applications beyond the laboratory. Entry 10 shows that the process remains effective on the 10-mmol scale (>99% selectivity for aniline and 82% isolated yield), suggesting that a large-scale lab procedure can be effected without a significant compromise in efficiency. The slightly reduced isolated yields compared to experiments with lower loadings of starting material are likely due to the longer reaction times necessary to drive complete conversion of the nitrobenzene in this unoptimized cell. These extended reaction times provide more opportunity for the product to diffuse into the anode compartment, thus reducing the aniline harvest from the catholyte (on which the isolated yields are based).

Meanwhile, entry 11 shows that the reference electrode (essential for controlling the cell potential in a proof-of-concept study such as this, but not usually applied in industrial electrochemical contexts) can be dispensed with. Hence in a two-electrode cell, >99%



**Figure 4. Electrocatalytic reduction of nitrobenzene to aniline using the phosphotungstic acid mediator in 4 consecutive full conversion cycles**

Phosphotungstic acid ( $9.74 \times 10^{-5}$  mol, 10 mol %) were dissolved in 30 mL 1 M aqueous  $\text{H}_3\text{PO}_4$  using the typical 2-compartment cell setup. 100  $\mu\text{L}$  of nitrobenzene was added at  $t = 0$  h and then periodically, as indicated by the arrows. 100  $\mu\text{L}$  of nitrobenzene ( $9.74 \times 10^{-4}$  mol) requires 564 C for the full 6-electron reduction to aniline, so the minimum theoretical charge required to reduce all 400  $\mu\text{L}$  of nitrobenzene is 2,256 C.

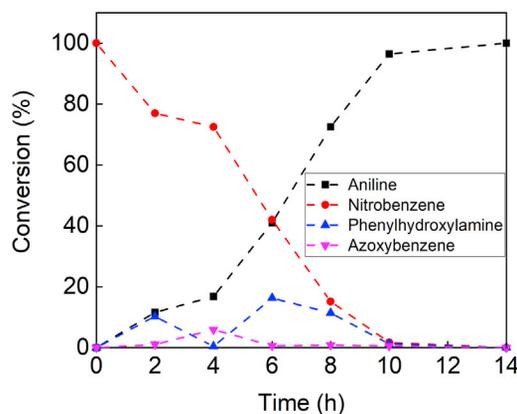
selectivity for aniline production can be achieved. While these conditions have not been optimized in terms of current density or cell design, the combination of these results (high selectivity at low mediator loadings, ability to tolerate operation under air, potential for scale-up and amenability to two-electrode operation) suggests that this approach could hold promise for the reduction of nitroarenes at preparative scale.

#### Repeated use of the polyoxometalate mediator

The results above suggest some versatility for this mediated electrocatalytic system for the selective reduction of different nitroarenes. Hence, we next tested the ability of the catalyst to perform multiple rounds of nitrobenzene reduction. For this purpose, a nitrobenzene reduction experiment was performed over the course of a week, with more nitrobenzene being periodically added into the working compartment of the cell. As shown in Figure 4, each of these aliquots of nitrobenzene was fully reduced to aniline without any other alterations to the ongoing reaction, showing that the mediator is able to function as part of a continuous cycle. The reduction profiles become somewhat less steep with successive cycles, which we believe is caused by some precipitation of the polyoxometalate mediator from the solution as the aniline product builds up (a white solid precipitate was noted at the end of the fourth cycle, which mass spectrometry showed to be phosphotungstic acid). Optimization of the reaction process (e.g., to a continuous flow system) could help to mitigate this issue. After extraction at the end of the fourth cycle, the  $^1\text{H}$  NMR of the resulting product showed >99% selectivity toward aniline with a 92% overall isolated yield for the reaction, within the range found for the single-pass experiments outlined in Table 3.

#### Reaction mechanism

To gain insight into the mechanism of nitroarene reduction in this mediated system, aliquots from ongoing (i.e., not yet complete) electrocatalytic reduction reactions of nitrobenzene were extracted and analyzed by  $^1\text{H}$  NMR spectroscopy, allowing the identification of three reaction intermediates: phenylhydroxylamine, azoxybenzene, and nitrosobenzene. Figure 5 shows a plot of the relative amounts of nitrobenzene, aniline, phenylhydroxylamine, and azoxybenzene present in the reaction medium at various different time points: phenylhydroxylamine and azoxybenzene were the



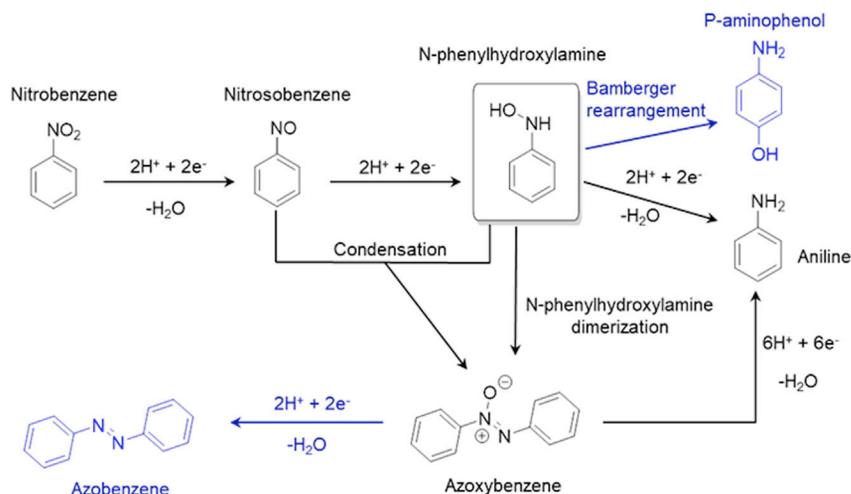
**Figure 5. The relative amounts of the various nitrobenzene-derived species detected in incomplete reaction mixtures as a function of time**

Typical reaction conditions were used;  $1.94 \times 10^{-4}$  mol of nitrobenzene was added to 30 mL of a 10% mol aqueous solution of phosphotungstic acid, and the reaction was subjected to a cathodic potential of  $-0.38$  V versus Ag/AgCl.

main intermediate species, while nitrosobenzene was only ever detected in trace amounts (specifically at  $t = 4$  h, not shown in the figure).

It is interesting to compare these data with the mechanism proposed by Marquez and Pletcher<sup>21</sup> for the direct electroreduction of nitrobenzene at an electrode surface under acidic conditions (which in Marquez and Pletcher's case gave rise predominantly to *p*-aminophenol, rather than aniline). The most obvious distinction is that in our process, *p*-aminophenol is never observed. Marquez and Pletcher proposed that nitrobenzene was reduced directly to phenylhydroxylamine, whereas the traces of nitrosobenzene that we observe would tend to suggest that this process happens through at least one intermediate step; namely, the two-electron reduction of nitrobenzene to nitrosobenzene, followed by a further two-electron reduction of that nitrosobenzene to phenylhydroxylamine. The fact that nitrosobenzene is only ever observed fleetingly in our studies (and not at all by Marquez and Pletcher) suggests that the onward reaction of nitrosobenzene is rapid.<sup>29</sup> Azoxybenzene was also observed in our reaction mixture, but only as an intermediate, whereas Marquez and Pletcher found this to be one of the end products of their reaction. There is some debate in the literature as to whether azoxybenzene can<sup>37,38</sup> or cannot<sup>25,27,39</sup> be converted to aniline electrochemically. In our case, we have been able to show unambiguously that azoxybenzene can be cleanly reduced to aniline by the 2-electron reduced phosphotungstic acid. This was achieved by reducing a solution of phosphotungstic acid of known concentration by two electrons per mediator molecule, and then adding this solution to azoxybenzene under an inert atmosphere in an "ex-cell" (i.e., non electrochemical) process (see [supplemental experimental procedures, SI-3.4](#)). Under such conditions (with roughly 8 equiv of the 2-electron reduced phosphotungstic acid present), azoxybenzene converts to aniline in a >99% yield. This suggests that one of the reasons for the excellent selectivity of our mediated process is that the reduced mediator is itself able to reduce azoxybenzene to aniline. Meanwhile, azobenzene was not identified as an intermediate in any of our experiments, although if it does form, then it too can be reduced to aniline by adding an excess of the two-electron reduced mediator in an ex-cell fashion (see [supplemental experimental procedures, SI-3.4](#)), implying that the reduced mediator in an electrocatalytic process would be able to reduce azobenzene to aniline as well.

The reaction mechanism for the electrochemical reduction of nitrobenzene that we think best explains our results ([Scheme 1](#)), mostly agrees with the one that has been reported previously for chemical reduction of nitrobenzene using reducing agents and metal catalysts.<sup>40,41</sup> Hence, nitrobenzene is reduced by two electrons to form nitrosobenzene, which is then reduced by another two electrons to form



**Scheme 1. Proposed mechanism for the electrocatalytic reduction of nitrobenzene to aniline mediated by phosphotungstic acid**

Processes shown with blue arrows indicate pathways that have previously been identified in other reports, but were not observed in this study.

phenylhydroxylamine. As [Figures S3](#) and [S4](#) show, both nitrosobenzene and phenylhydroxylamine display quasi-reversible redox waves, the reductive parts of which have peaks at +0.2 V versus Ag/AgCl (for nitrosobenzene) and +0.1 V versus Ag/AgCl (for phenylhydroxylamine). This suggests that these two species are both relatively easy to reduce under the prevailing conditions, either at the electrode surface or on contact with reduced phosphotungstic acid. The latter assumption is borne out by ex-cell reactions between phenylhydroxylamine and 1-electron reduced phosphotungstic acid (see [supplemental experimental procedures, SI-5](#) and [Figure S12](#)), whereby two equivalents of 1-electron reduced phosphotungstic acid can reduce phenylhydroxylamine to aniline with a yield of approximately 90% (full conversion can be achieved if excess 1-electron reduced phosphotungstic acid is used).

However, a cyclic voltammogram of nitrobenzene itself ([Figure S5](#)) presents a rather different picture, displaying a single irreversible reduction wave at approximately  $-0.5$  V versus Ag/AgCl. The presence of nitrosobenzene and phenylhydroxylamine in the reaction mixture, and their apparent ease of reduction, therefore suggest that it is the initial reduction of nitrobenzene to nitrosobenzene that is especially challenging during direct reduction at the electrode surface, requiring potentials as cathodic as  $-0.5$  V. Once nitrosobenzene has formed, it will be rapidly reduced at those potentials to phenylhydroxylamine. Phenylhydroxylamine can be further reduced at those potentials to aniline, but it also has a tendency to undergo reaction with nitrosobenzene to give azoxybenzene, and/or to dimerize (also giving azoxybenzene). Under direct electrolysis conditions, where large cathodic potentials are applied to drive the initial reduction of nitrobenzene, there is likely to be a high local concentration of both nitrosobenzene and phenylhydroxylamine at the electrode surface and this is likely to lead to a considerable loss of selectivity for aniline production by the generation of azoxybenzene. Azoxybenzene is poorly soluble in aqueous solution (only  $\sim 1$  mg is dissolved per liter at 293 K), and its precipitation, if it forms in significant amounts, may account for some of the conflicting reports in the literature as to whether it is an end product of nitrobenzene reduction.

The above discussion explains why the cyclic voltammogram of nitrobenzene (Figure S6) has only one large irreversible wave (as after the initial reduction to nitrosobenzene, subsequent steps are facile and rapid) and also why direct reduction processes produce azoxybenzene. The redox mediator in our system is therefore acting to increase the selectivity of the reaction in at least three ways. First, the mediator acts to lower the cathodic potential necessary for initial nitrobenzene reduction (Figure 2; Table 3), perhaps by presenting both protons and electrons to the nitrobenzene simultaneously and thereby bypassing high-energy intermediates. Previous models of nitrobenzene reduction to nitrosobenzene have invoked an initial one-electron, one-proton reduction to the anion  $\text{ArN}(\text{OH})\text{O}^-$ , which then undergoes further (possibly stepwise) protonation and reduction to yield nitrosobenzene.<sup>42</sup> Were such a stepwise mechanism to operate at the electrode surface, it is likely that this would impede the kinetics of reduction; in contrast, as a soluble source of both protons and electrons, the reduced polyoxometalate mediator may be able to circumvent some of these kinetic barriers through a proton-coupled-electron transfer mechanism.<sup>43</sup> Second, the reduction reactions mediated by the polyoxometalate mediator are occurring in bulk solution, as opposed to direct electrochemical reduction, which necessarily occurs at the electrode surface. In bulk solution, the concentrations of nitrosobenzene and phenylhydroxylamine will be much lower than they are at the electrode surface during direct reduction. This means that the mediated system is much less prone to the coupling reactions between nitrosobenzene and phenylhydroxylamine (and/or phenylhydroxylamine dimerization) that form azoxybenzene. Third, even if azoxybenzene does form, the reduced polyoxometalate mediator is capable of cleanly reducing this to aniline.

It is interesting to compare this mechanism with those for direct reduction of nitrobenzene at the electrode surface. In regard to direct reduction at the electrode, different electrolyte pH and cathode materials can lead to the formation of different products,<sup>39,44–47</sup> while in general, the applied potential is held to alter the ratio of these products.<sup>48,49</sup> *p*-Aminophenol (the main product of Marquez and Pletcher's study<sup>21</sup>) most likely forms from phenylhydroxylamine via the Bamberger rearrangement. *p*-Aminophenol was also identified as the major reduction product (with aniline being completely absent) under bulk electrolysis at  $-0.37$  V versus Ag/AgCl in a comprehensive study on the effect of the applied potential on nitrobenzene reduction in acidic media at a Hg cathode published by Harwood et al.<sup>48</sup> Only as the potential was made more cathodic ( $-0.77$  V versus Ag/AgCl) were significant amounts of aniline formed (50% maximum yield), and variable amounts of side products such as *p*-aminophenol, azoxybenzene, and *p*-phenetidine were found at all of the different applied potentials.<sup>48</sup> Moreover, simply making the reaction potential more cathodic in the hope of promoting aniline formation has its limits, as increasingly cathodic potentials facilitate competing hydrogen evolution, and the tendency to overreduction (e.g., to cyclohexylamine) also increases. Hence, we postulate that the origin of the poor selectivity for aniline in many of the previous reports on electrochemical nitrobenzene reduction arises largely through the difficulty in controlling the reactivity of the phenylhydroxylamine intermediate at the potentials that are required to reduce nitrobenzene directly at an electrode surface.<sup>48,50,51</sup> In contrast, the mediated approach expounded here avoids a significant buildup of phenylhydroxylamine and hence prevents any significant flux through the Bamberger rearrangement to *p*-aminophenol. Experiments in which *p*-aminophenol was reacted in an ex-cell fashion with 10 equiv of 2-electron reduced phosphotungstic acid failed to yield any conversion to aniline after stirring at room temperature for 12 h. This suggests that *p*-aminophenol does

not form at all in our mediated route (or else we would observe it in our product mixtures) and instead that its formation is prevented.

Here, we have described a highly selective route for the electrochemical reduction of nitroarenes to their corresponding anilines. The procedure is simple and potentially more sustainable than traditional routes, avoiding the use of hydrogen gas, high temperatures, precious metal co-catalysts and sacrificial reagents. Instead, the approach described in this work proceeds in aqueous solution at room temperature and pressure, with the electrons and protons required to reduce the nitrobenzenes originating from water. Faradic efficiencies are typically greater than 90%, even for catalyst loadings as low as 0.1% relative to the nitroarene starting material, and the selectivity for the aniline product is near-quantitative, even under an atmosphere of air. With the aid of various control reactions and mechanistic studies, we propose a reaction pathway that explains why this electro-mediated approach gives such superior conversion and selectivity compared to direct electrochemical reduction of the substrates at the electrode surface, and we show that our mild electrocatalytic conditions allow the clean and efficient conversion of sensitive nitrobenzene substrates such as ortho-iodides to their aniline derivatives in good yield. Given the scale and environmental impact associated with the production of anilines, this electrochemical route could hold considerable promise for the development of more sustainable processes for the production of these vital chemical feedstocks.

## EXPERIMENTAL PROCEDURES

### Resource availability

#### Lead contact

The lead contact for this article is Mark Symes ([mark.symes@glasgow.ac.uk](mailto:mark.symes@glasgow.ac.uk)).

#### Materials availability

No unique reagents were generated by this study.

#### Data and code availability

The data underpinning this study have been deposited in the University of Glasgow's Enlighten database under accession code <https://doi.org/10.5525/gla.researchdata.1279>.

## SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.xcrp.2022.100914>.

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## AUTHOR CONTRIBUTIONS

A.D.S. performed the experiments and analyzed the data. M.D.S. conceived the idea, assisted with the data analysis, and supervised the project. A.D.S. and M.D.S. co-wrote the manuscript.

## DECLARATION OF INTERESTS

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