Supplementary Information (SI) for Reaction Chemistry & Engineering.

Supporting Information

Technoeconomic analysis of fine chemical electrosynthesis: A case study using electrooxidation of 2-methylnaphlene to Vitamin K_3

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1. The details for calculating the cost per mole of electrons

1.1 The method to calculate the cost per mole of electrons for electricity

$$Cost = W * Price_{Electricity}$$

$$W = \frac{I * t * U}{FE}$$

$$Q = I * t$$

$\boldsymbol{W}$ is the amount of electrical energy required to supply 1 mol of electrons, $\boldsymbol{I}$ is the current needed to pass 1 mol of electrons, $\boldsymbol{t}$ is the time needed to pass 1 mol of electrons, $\boldsymbol{U}$ is the voltage, which is assumed to be 5V, and $\boldsymbol{FE}$ is the Faradaic efficiency of the reaction, which is assumed to be 100%, $\boldsymbol{Q}$ is the charge of 1 mol of electrons (96485 C).

1.2 The method to calculate the cost per mole of electrons for 30% NaClO solution

$$Cost = \frac{m * Price_{30\%\ NaClO\ solution}}{n}$$

$$m = \frac{M_{Cl2}}{10\%}$$

m is the weight of 30% NaClO solution required to provide 1 mol available chlorine (Cl_2). 10% is the available chlorine in 30% NaClO solution. M_{Cl2}(70.9 g/mol) is the molar mass of Cl_2, n(2) is the number of moles of electrons contained in 1 mole of Cl_2. $Price_{30\%\ \mathrm{NaClO\ solution}}$ is $63.38 per ton (www.chemicalbook.com).

1.3 The method to calculate the cost per mole of electrons for Zn

$$Cost = \frac{M_{Zn} * Price_{\mathrm{Zn}}}{n}$$

M_{Zn}(65.4 g/mol) is the molar mass of Zn, and n(2) is the number of moles of electrons contained in 1 mole of Zn. $Price_{\mathrm{Zn}}$ is $2943 per ton (www.lme.com).

2. The details for calculating the cost corresponding to the production of each ton of 2-MNQ

The total electrolysis cost $(Cost_{Total})$ corresponding to the production of each ton of 2-MNQ consists of the electrolysis hardware cost $(Cost_{Hardware})$ and electricity cost $(Cost_{Electricity})$

$$Cost_{Total} = Cost_{Hardware} + Cost_{Electricity}$$

the cost of hardware $(Cost_{Hardware})$ was calculated by

$$Cost_{Hardware} = Cost_{Equipment} + Cost_{Anode} + Cost_{Cathode} + Cost_{Membrane}$$

equipment refers to industrial electrolysis equipment excluding electrodes and ion exchange membranes.

$$Cost = \frac{Price * Area}{Lifespan * Annual\ putout}$$

where $Lifespan$ refers to the period during which various devices operate normally, the $Area$ refers to the area required for electrodes, separators, cathodes, anodes, and equipment under annual production conditions) was calculated by

$$Area = \frac{Q_{Annual\ putout}}{J * t * FE}$$

where the $Q_{Annual\ putout}$, The annual electricity consumption required for the production of 2-MNQ), was calculated by

$$Q_{Anual\ putout} = \frac{Annual\ putout * F}{M_{2-MNQ}}$$

where F is 96485 C/mol, t is the time in seconds of 1 year, J is the current density, FE is Faradaic efficiency, and M_{2-MNQ} is the molar mass of 2-MNQ (172.18 g/mmol).

Based on the aforementioned relationship, we have determined that under the assumption of annual production conditions, the $Area$ is related to both the current density (J) and the Faradaic efficiency (FE). In this study, we investigated the relationship between FE and different current densities (J). Consequently, we conducted an empirical fit within the tested range $f_1(J)$. As a result, the $Area$ can be expressed as a function of the current density, allowing us to ultimately convert the $Cost_{Hardware}$ into a function dependent on current density $f_2(J)$.

Based on our assumed production yield and the collected relevant pricing data, we derived the empirical functional relationship as follows:

$$FE = f_1(J) = 0.4446 * e^{\left(-\frac{J}{186.13}\right)} + 40.74$$

$$Cost_{Hardware} = f_2(J) = \frac{73070.7}{J * (0.4446 * e^{\left(-\frac{J}{186.13}\right)} + 40.74)}$$

the cost of electricity $\left(Cost_{Electricity}\right)$ was calculated by

$$Cost_{Electricity} = I * U * t * Price\ of\ Electricity$$

where the I is the current during the electrooxidation of Ce^{3+}, the U is cell voltage, t is the time in seconds for production of 1 ton of 2-MNQ. In this study, we investigated the relationship between U and different current densities. Consequently, we conducted an empirical fit within the tested range $f_3(J)$. As a result, the U can be expressed as a function of the current density, allowing us to ultimately convert the $Cost_{Electricity}$ into a function dependent on current density $f_4(J)$.

Based on our assumed production yield (60%) and the collected relevant pricing data, we derived and simplified the empirical functional relationship as follows:

$$FE = f_3(J) = -5.69 * e^{\left(-\frac{J}{555.41}\right)} + 7.444$$

$$Cost_{Electricity} = f_4(J) = \frac{252.2 * (-5.69 * e^{\left(-\frac{J}{555.41}\right)} + 7.444)}{\left(0.4446 * e^{\left(-\frac{J}{186.13}\right)} + 40.74\right)}$$

and the $Percent$ of electricity cost ($Cost_{Electricity}$) in total electrolysis cost ($Cost_{Total}$) could be calculated by

$$Percent(\%) = \frac{Cost_{Electricity}}{Cost_{Hardware} + Cost_{Electricity}}\%$$

3. The details for calculating the cost of the reagent and electrolysis to the production of each ton of 2-MNQ for Table 1

3.1 The details for calculating the cost of the reagent

The daily output is 1.33 tons, based on an annual production of 400 tons of 2-MNQ over 300 working days per year. The cost of reagents for each ton of 2-MNQ were calculated by

$$Cost = \frac{N_a * M_a}{N_{2-MNQ} * M_{2-MNQ} * Yield} * Price * (1 - rate\ of\ recovery)$$

where N_a is the reaction equivalence and M_a is the molar mass. The equivalence of 2-MN is 1. The equivalence of $Ce_2(CO_3)_3 \cdot xH_2O$ is 5 by the ratio of Ce^{4+} to 2-MN base on experimental results. The equivalence of $MeSO_3H$ is 50.6 based on the amount of $MeSO_3H$ used in the preparation of the electrolyte. The equivalence of DCE is 74 was calculated based on the amount of DCE used in the oxidation experiment. M_{2-MN} is 142.1 g/mol, $M_{Ce2(CO3)3\cdot 8.5H2O}$ is 613.2 g/mol (contains 30% water), M_{MeSO3H} is 96.1 g/mol, M_{DCE} is 98.9 g/mol, M_{2-MNQ} is 172.18 g/mol, yield is 60%. The recycling recovery rates were 97% for $Ce_2(CO_3)_3 \cdot 8.5H_2O$, 99% for $MeSO_3H$, and 98% for DCE.

3.2 The details for calculating cost of hardware

The cost of hardware was calculated by

$$Cost_{Hardware} = \frac{Price * Area}{Lifespan * Anual\ putout}$$

the $Area$ was calculated by

$$Area = \frac{Q_{Anual\ putout}}{J * t * FE}$$

$$Q_{Anual\ putout} = \frac{Anual\ putout * F}{M_{2-MN}}$$

where F is 96485 C/mol, t is the time in seconds of 1 year, J is 50mA/cm^2 base on experimental results, FE is 90%, and the value of $Area$ is 256.2 m^2 by calculation.

Equipment refers to industrial electrolysis equipment excluding electrodes and ion exchange membranes. It includes necessary control equipment, temperature control equipment, circulation pumps, and other related devices for electrolysis. control equipment, temperature control equipment, circulation pumps, and other related devices for electrolysis.

3.3 The details for calculating cost of electricity

The cost of electricity was calculated by

$$Cost_{Electricity} = \frac{Price*U*J*S*t}{Anual\ putout},$$

where the price of electricity is \$0.1/kWh, U is 2.2 V based on experimental results, J is 50 mA/cm^2, S is 256.2 m^2, and t is the time in seconds of 1 year.

4. The details of 840 mL scale oxidation of 2-MN and the large-scale electrochemical cell setup

The diagram below shows the setup for the scale-up oxidation experiment of 2-MN. The reaction apparatus is a 2000 mL jacketed reactor, where the materials are mixed through mechanical stirring, and a temperature control unit is used to maintain a constant system temperature (Fig S1).

Fig. S1 Digital photograph 840 mL scale oxidation of 2-MN with Ce^{4+}. The reaction condition: 2-MN (24 mmol) in 240 mL DCE reacted with 600 mL of 0.4 M Ce^{4+} aqueous solution (containing 3.5 M H^+ and 4.6 M $MeSO_3^-$) at 65°C, 1000 RPM, for 3h.

The diagram below shows the structural schematic and component photographs of the designed electrochemical apparatus (Fig S2 and S3).

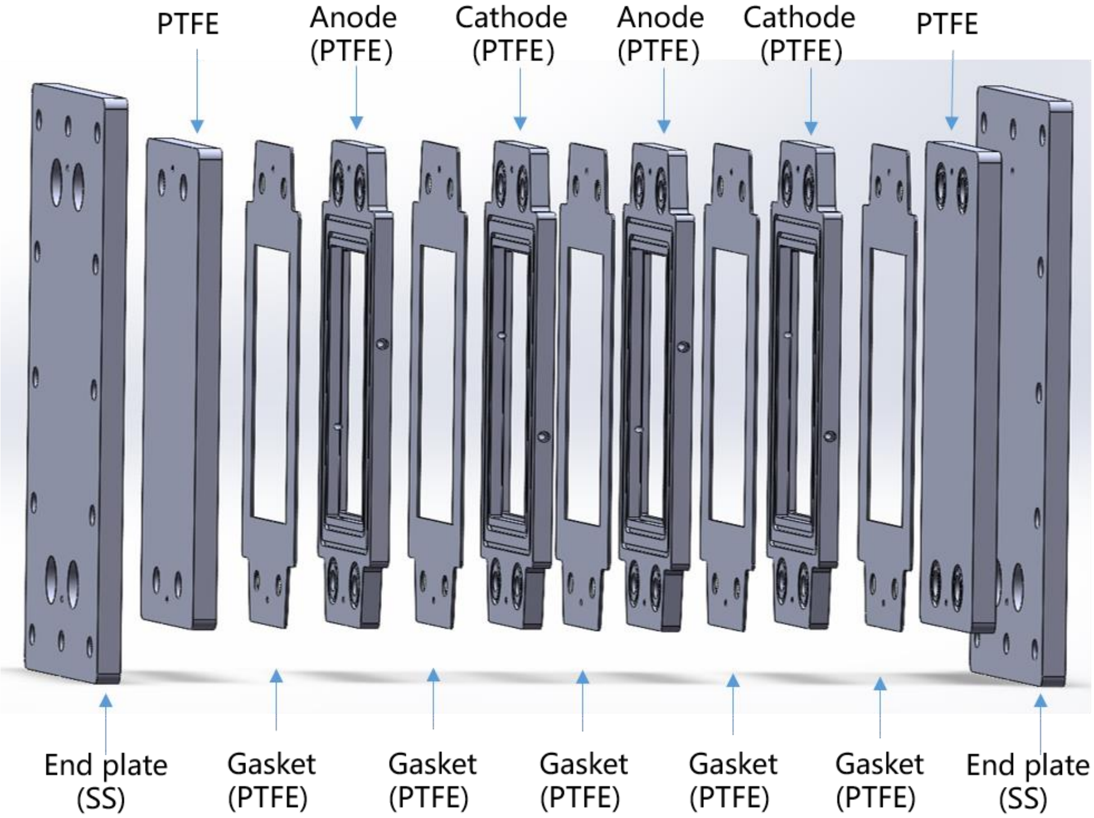


Fig. S2 Diagram of the large-scale flow electrolytic cell structure.

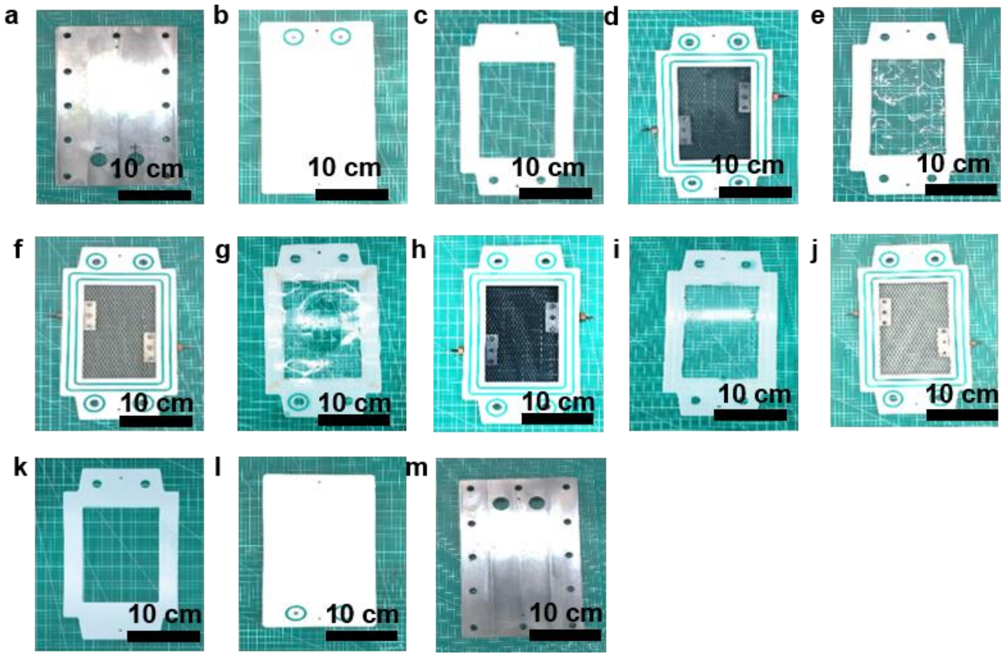


Fig. S3 Components of the large-scale flow electrolytic cell structure : a/m: stainless steel back plate; b/l: PTFE back plate; c/k: PTFE gasket; e/g/i: Nafion 117 ion-exchange membrane; d/h: 104 cm² DSA-coated titanium anode; f/j: 104 cm² platinum-coated titanium cathode.

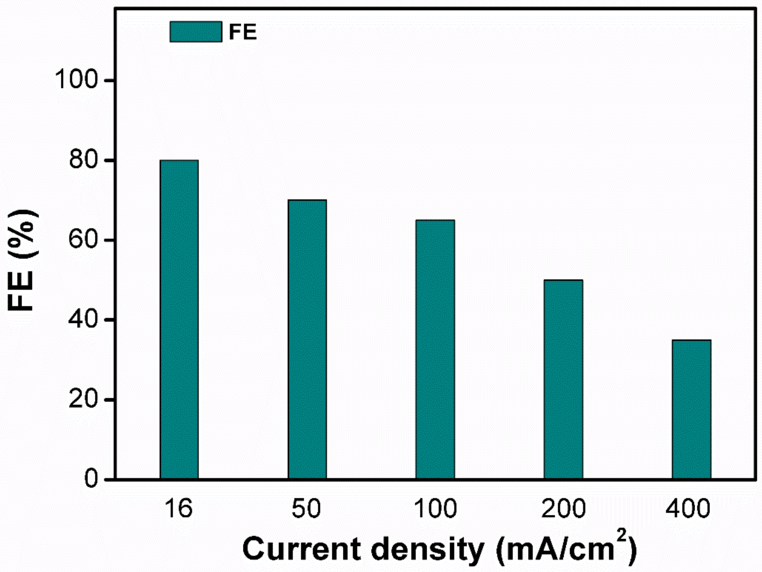


Fig. S4 The relationship current density vs. FE. in the batch without membrane. Testing condition: 1 cm^2 DSA anode, 1 cm^2 Pt mesh cathode. The anolyte and catholyte were 80 mL aqueous solutions containing 0.725 M Ce^{3+}, 5.9 M H^+, 8.1 M $MeSO_3^-$.

5. Procedure for cerium salt recovery

To evaluate the feasibility of the proposed approach, we conducted experiments on cerium salt recovery. After the reaction was completed, the mixed solution underwent extraction and separation, achieving 98% recovery in the aqueous phase. These results demonstrate the viability of this experimental approach.

6. Study of synthesis of 2-MNQ in a single step

We initially performed cyclic voltammetry (CV) for 2-MN in DCE solution and Ce in $MeSO_3H$ solution, as shown in Figures S5 and S6. The oxidation peak of 2-MN was observed at 0.99 V vs Ag/AgCl, while the onset of Ce(III) oxidation occurred at 1.28 V. This indicates that 2-MN would undergo direct oxidation in a single step.

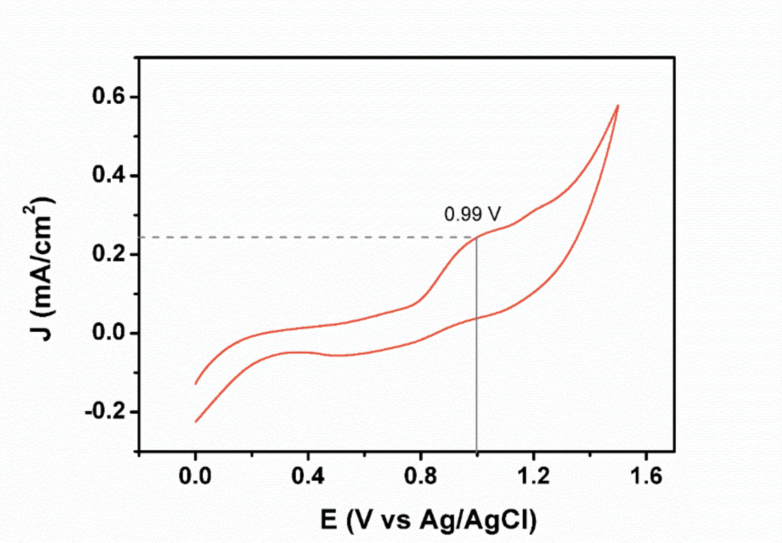


Fig. S5 Cyclic voltammetry curve of 2-MN in DCE solution. The electrolyte was an DCE solution containing 0.05 M 2-MN, 0.1 M Bu_4NBF_4. The anode is a 1 cm x 1 cm DSA, the cathode is 1 cm x 1 cm Pt mesh, the scan rate is 100 mV/s.

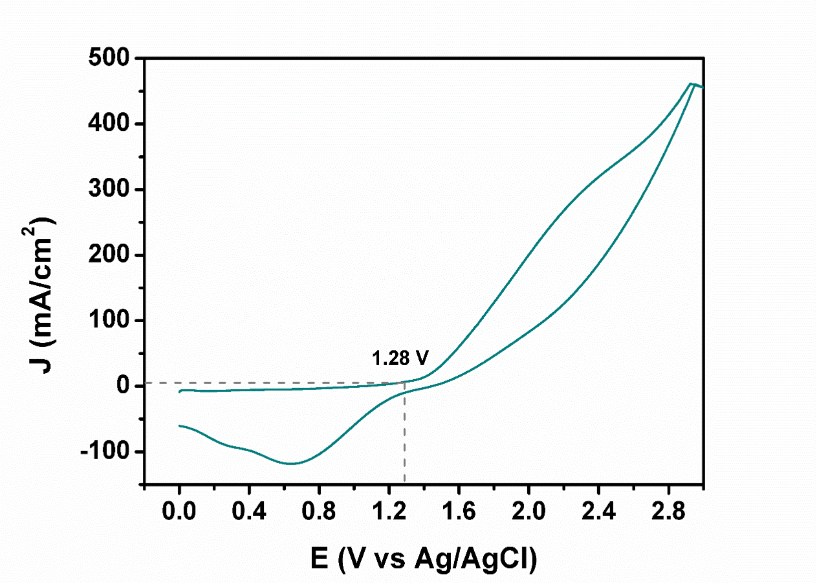


Fig. S6 Cyclic voltammetry curve of Ce(III). The electrolyte was an aqueous solution containing 0.725 M Ce^{3+}, 5.9 M H^+, and 8.1 M $MeSO_3^-$. The anode is a 1 cm x 1 cm DSA, the cathode is 1 cm x 1 cm Pt mesh, the scan rate is 100 mV/s.

We also conducted direct electrolysis experiments for the preparation of 2-MNQ with initial cerium salt to 2-MNQ ratios of 1 and 10, a current density of 50 mA/cm^2. After the reaction, the yield was analyzed by GC-MS. It was found that with an initial cerium salt(III) to 2-MNQ ratio of 1, the yield of 2-MNQ was only 2.76% (Table S1), and the conversion rate of 2-MN was 4.6%. With an initial cerium salt(III) to 2-MNQ ratio of 10, the yield of 2-MNQ was 23.7%, and the conversion rate of 2-MN was 78.3%.

Table S1 Result of the synthesis of 2-MNQ in a single step

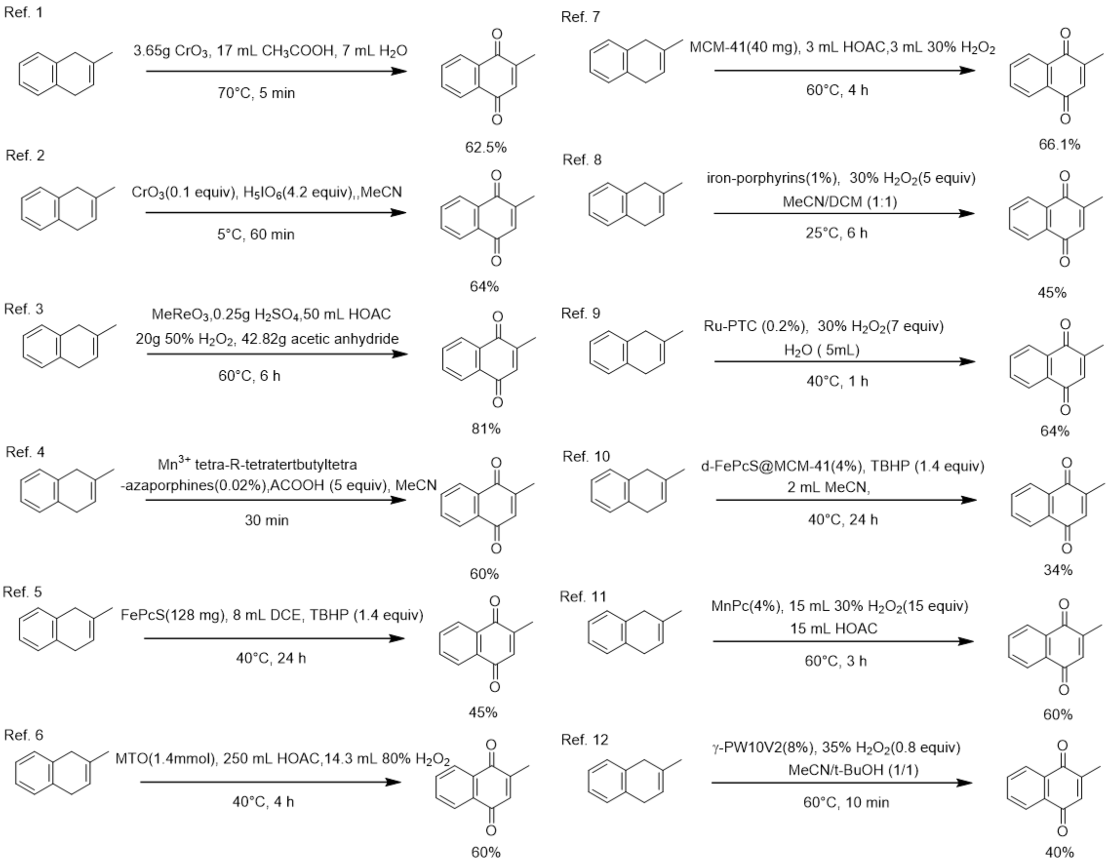
Ratio of Ce(III)/2-MN	Temp. (℃)	Time (s)	Current density (mA/cm^2)	Conversion (%)	Yield(%)
1	60	19297	50	4.6	2.8
10	60	19297	50	78.3	23.7

The reaction condition:2-MN (1 mmol, 142.2 mg) dissolved in 10 mL DCE was mixed with 2.5 or 25 mL of the prepared 0.48 M Ce^{4+} solution (containing 0.48 M Ce^{3+}, 3.9 M H^+, and 5.3 M $MeSO_3^-$). A undivided batch cell with a DSA anode (1 cm^2) and a platinum mesh cathode (1 cm^2). Allow the mixture to react at 60 °C under 1000 rotations per minute (RPM) magnetic stirring. The pass charged was 10 F. The electrolysis was performed with CHI 760E potentiostat.

7. Summary of existing methods for 2-MNQ synthesis

The table below summarizes the data on the oxidation of 2-MN to produce 2-MNQ in recent years. The yield reported in this paper falls within the higher-performing category (Table S2).

Table S2. Summary of the synthesis of 2-MNQ of the existing methodologies



8. Study on the formation mechanism of by-products in the reaction

The reaction selectivity was 71.4%, with the main byproduct being 6-methyl-1,4-naphthoquinone, along with a small amount of binaphthyl products (Fig. S7). The formation of 6-methyl-1,4-naphthoquinone occurs because, during the oxidation of the benzene ring near the methyl group to form 2-MNQ by Ce(IV) ions, the benzene ring distant from the methyl group is also oxidized, leading to the byproduct 6-methyl-1,4-naphthoquinone. The formation of binaphthyl is due to the oxidation by Ce(IV) ions, which abstracts a hydrogen atom from the benzene ring, generating radical species. The coupling of two such radicals leads to the formation of the binaphthyl byproduct (Fig. S8).

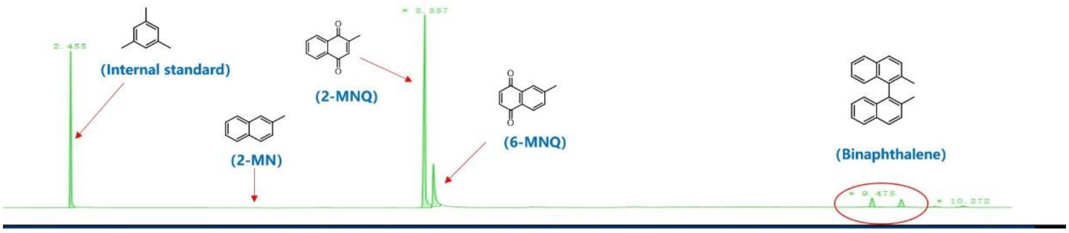


Fig. S7 GC spectra after the oxidation reaction.

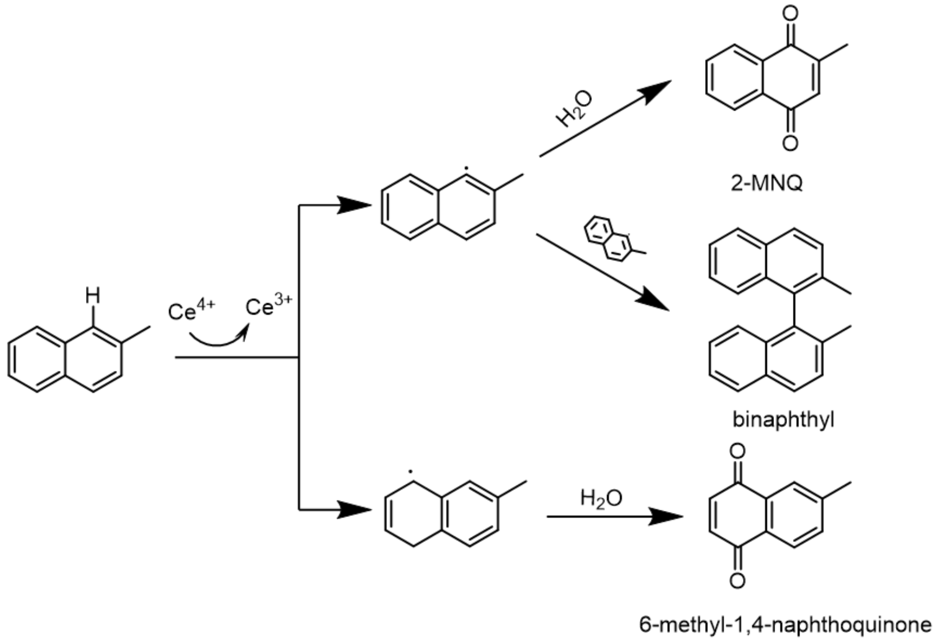


Fig. S8 The possible mechanism for by-product formation.

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