

Supplementary Information

Cobalt phthalocyanine (CoPc) anchored on Ti₃C₂ MXene nanosheets for highly-efficiently selective catalytic oxidation

Simeng Zhu^a, Peng Liu^b, Xinlin Hong^{a*}

^aCollege of Chemistry and Molecular Sciences, Wuhan University, Wuhan, China

^bHubei Province Engineering and Technology Research Center for Fluorinated Pharmaceuticals,

Wuhan University, School of Pharmaceutical Sciences, Wuhan University, Wuhan, China

Experimental Procedures:

SI.1 CoPc Synthesis

All commercially available chemicals were used without further washing. For the synthesis of CoPc, 5.76 mmol of phthalonitrile (Sigma-Aldrich), 1.44 mmol of cobalt(II) acetate tetrahydrate (Merck), and 10 mg of ammonium heptamolybdate tetrahydrate (Merck) catalyst were put in 250 mL three necked flask with ethylene glycol solvent and stirred for 30 min. Heat in an oil bath at 200 °C for 16 hours. After the reaction is completed, allow the reactant to cool to room temperature. Dilute and filter with anhydrous ethanol. Wash the filter cake with a 2% wt NaOH alkaline solution and hydrochloric acid solution, and then wash with ultrapure water until neutral. Dry the crude product under vacuum at 80 °C for 12 hours, cool it, grind it into powder, soak it in 6 mol/L hydrochloric acid for 12 hours, filter it, and wash it with deionized water until the pH is close to neutral and there are no free cobalt ions. The product is vacuum dried at 80 °C for 12 hours, followed by acetone as solvent and Soxhlet extraction until the solvent is colorless and clear. The filter paper is then taken out and dried naturally in a fume hood to minimize the evaporation of acetone. Finally, cobalt phthalocyanine is obtained by vacuum drying at 80 °C for 12 hours.

S1.2 Catalytic Oxidation Reaction Experiments

The experimental setup for the production of quinclorac from 3,7-dichloro-8-dichloro methyl quinoline (3,7-D-8-DMQ) oxidized by oxygen is demonstrated. The oxidation reaction is carried out in a 60 mL sealed high-pressure autoclave. The oscillation in the reaction temperature was maintained within ± 0.2 °C by an electric heater with a thermocouple. The change in pressure in the autoclave was adjusted within 0.02 bar by a regulator.

The oxidation of 3,7-D-8-DMQ to quinclorac was performed as follows. The autoclave was filled with a mixture of the proposed amounts of acetic acid (0.17 mol), 3,7-D-8-DMQ (0.1 mmol), CoPc/Ti₃C₂-X (0.08 mmol), manganous acetate (0.02 mmol) and hydrobromic acid (1.6 mmol). The concentration of HBr solution is 40%. O₂ was introduced into the autoclave to replace air in the reaction system and the pressure in the autoclave was increased to the desired value. An airtight-ness test of the setup was made by maintaining the scheduled pressure for 5 min. Agitation was then started and the temperature of the autoclave was raised gradually if the setup was shown to have excellent airproof performance. The oxidation reaction began as soon as the scheduled temperature was attained. A sample was taken from the autoclave every 1 h to determine the concentrations of quinclorac and 3,7-D-8-DMQ.

After each cycling test, the catalyst was washed and dried for stability testing (6 h for each cycle). The re-usability of CoPc/Ti₃C₂ catalyst has been studied via catalytic experiments using the recovered CoPc/Ti₃C₂ samples.

S1.3 Analytical methods

A high-performance liquid chromatography (HPLC) method was established to determine 3,7-D-8-DMQ and quinclorac with a C18 steel column. The mobile phase consisted of methanol and 0.4 (wt)% H₃PO₄. In the first 5 min, the flowrate of the mobile phase was 0.8 mL/min with a CH₃OH/H₃PO₄ ratio (flow rate) of 1.5. In 5–10 min, the liquid flow increased to 1.0 mL/min and the CH₃OH/H₃PO₄ ratio was raised to 4. In 10–25 min, the CH₃OH/H₃PO₄ ratio and the liquid flow rate were maintained

constant. 3,7-D-8-DMQ and quinclorac were tested using an ultraviolet detector at 220 nm. The standard profiles of 3,7-D-8-DMQ and quinclorac were acquired by standard solution. The standard equations obtained by least squares are shown in Table 1, where X stands for area and Y represents the concentration of the component, with units of 10^{-6} g/mL. Quinclorac yield was calculated as follows.

$$C_a = \frac{m_0 - m_a}{m_0} \times 100\%$$

$$S_q = \frac{m_a \times M_a}{(m_0 - m_a) \times M_q} \times 100\%$$

$$Y_q = C_a \times S_q$$

where C_a stands for the conversion of 3,7-D-8-DMQ, S_q stands for the selectivity of quinclorac and Y_q stands for the yield of quinclorac.

51.4 Materials Characterization

A Cary-100 spectrophotometer was used to record the UV–vis diffuse reflectance spectra. The thickness and surface topology for the samples were determined using an atomic force microscopy (AFM, Multimode 8 AFM, Bruker, Germany) under Scan Analyst mode with cantilevers at a spring constant of 0.35 N m^{-1} and a frequency of 65 kHz. Field emission scanning electron microscope (JSM-7500F, JEOL, Japan) was applied to determine the morphologies of the prepared samples. Oxford Instruments X-ray analysis system equipped on JSM-7500F was used to carry out the energy-dispersive X-ray (EDX) spectroscopy and elemental mapping test. Titan G2 60–300 microscope operated at 300 kV was used to obtain the transmission electron microscope (TEM) images of the prepared samples. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo Scientific X-ray Photoelectron Spectrometer with a monochromatic Al $K\alpha$ source with an energy of 1486.6 eV and operating power of 225 W (15 kV, 15 mA). The radical signals and reactive intermediate species were recorded on an electron paramagnetic resonance (EPR) spectrometer (JES-FA200).

Figures

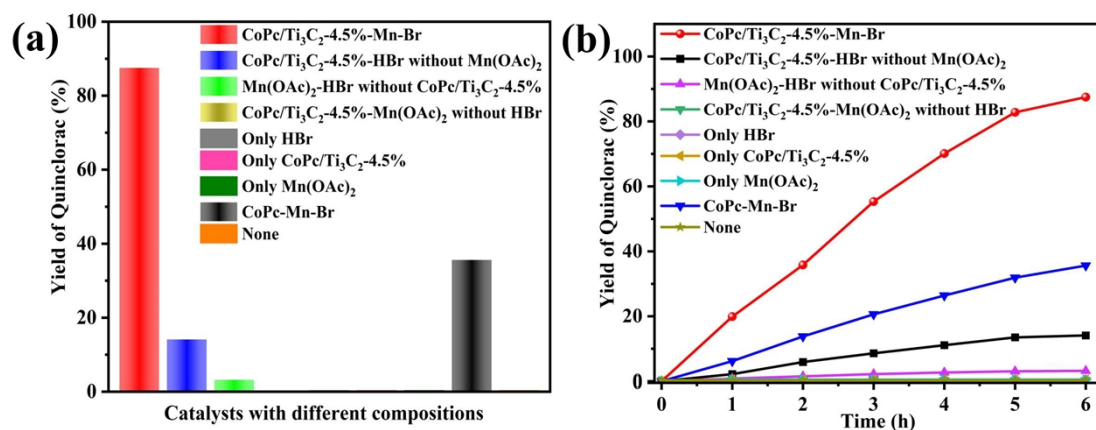


Fig. S1. Control experiments: Influence of different components on the yield of quinclorac during the catalytic oxidation reaction.

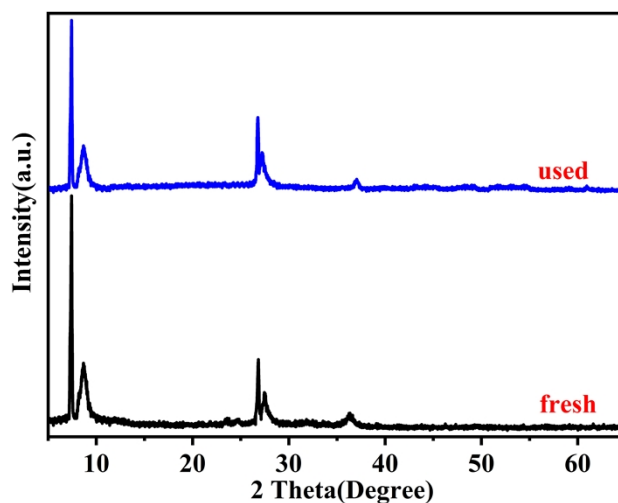


Fig. S2. XRD patterns of the CoPc/Ti₃C₂-4.5% before and after 5 times stability test.

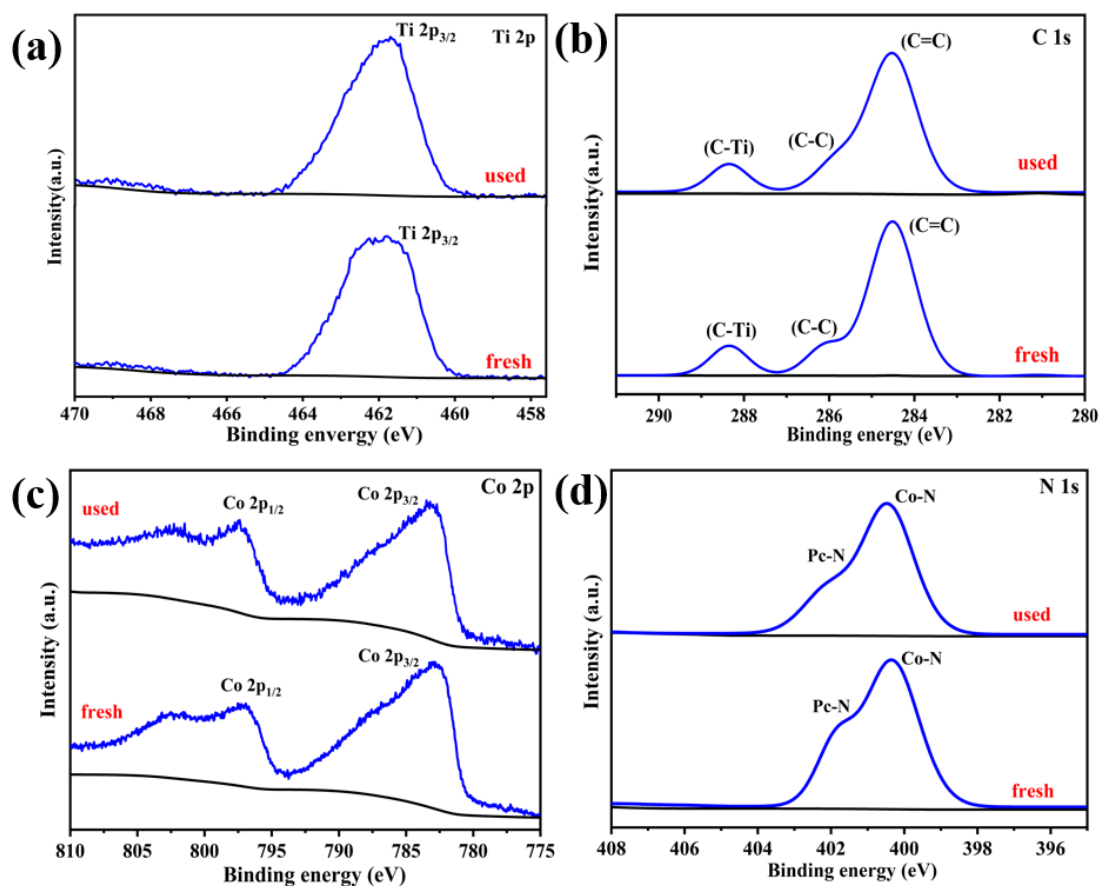
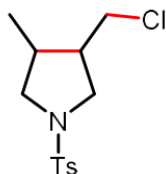


Fig. S3. X-ray photoelectron spectroscopy spectra of Ti 2p (a), C 1s (b), Co 2p (c) and N 1s (d) of CoPc/Ti₃C₂-4.5% before and after 5 times stability test.



3-(chloromethyl)-4-methyl-1-tosylpyrrolidine, 1:0.5 diastereomers. Yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.77 – 7.68 (m, 2H+1H), 7.40 – 7.30 (m, 2H+1H), 3.57 – 3.39 (m, 3H+1.5H), 3.34 (dd, J = 11.1, 7.5 Hz, 0.5H), 3.25 – 3.11 (m, 2H+0.5H), 3.04 (dd, J = 9.8, 4.9 Hz, 1H), 2.83 (dd, J = 9.8, 8.0 Hz, 0.5H), 2.48 – 2.28 (m, 3H+3.5H), 2.04 – 1.94 (m, 1H), 0.98 (d, J = 6.4 Hz, 1.5H), 0.86 (d, J = 6.9 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 143.6, 143.5, 133.8, 133.4, 129.7, 127.6, 127.5, 54.8, 54.4, 51.3, 50.1, 47.8, 44.9, 44.4, 42.7, 36.4, 34.9, 21.6, 16.7, 12.8. **GC-MS** (EI, m/z) for C₂₂H₂₉N₃S₃ Calcd: 287.1, 289.1, found: 287.0, 289.0. Spectra data are consistent with the reported literature.

Fig. S4. Characterization data for the controlled experiment of cyclochlorinated compound.

Table S1. Comparison of CoPc/Ti₃C₂-Mn(OAc)₂-HBr catalyst with these previously reported homogeneous Co-based catalysts.

Catalyst	Quinclorac yield (%)	Ref.
CoPc/Ti ₃ C ₂ -4.5%-Mn-Br	87.5	This work
Sulfuric acid/Nitric acid	52.5	[1]
Co(OAc) ₂ -Mn(OAc) ₂ -HBr	54.2	[2]
H ₃ PMo ₁₂ O ₄₀ /Ce/Co/Br	61.8	[3]

References

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- [2] W. Xu, M. Wei, W. Zang, G. Yu, G. Zhou, A methods for the synthesis and purification process for preparing 3,7-dichloro-8-quinolinecarboxylic acid. *CN Patent*, 2010, **101851197A**.
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