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Single crystalline MnOOH nanotubes for selectively oxidative coupling of anilines to aromatic azo compounds

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1. Experimental section

1.1. Preparation of catalysts

1.1.1. Synthesis of NT-MnOOH

In a typical synthetic process of γ -phase NT-MnOOH, 1.0 g of KMnO₄ was dissolved in 36.0 mL of the mixed water/ethanol solvent with ethanol volume percentage of 5%. Then, the mixture was transferred into a 100 mL Teflon lined autoclave. Afterwards, the autoclave was sealed and reacted at 140 °C for 8 h. As-synthesized NT-MnOOH were washed by deionized water for three times and dried at 70 °C for 12 h.

The series of NT-MnOOH-t catalysts were also prepared through the same process expect the various hydrothermal reaction times.

1.1.2. Synthesis of NW-MnOOH

For synthesis of γ -phase NW-MnOOH, 0.25 g of KMnO₄ was dissolved in 36.0 mL of the mixed water/ethanol solvent with ethanol volume percentage of 2%. Then, the mixture was hydrothermally treated at 140 °C for 12 h. As-synthesized NW-MnOOH were washed by deionized water for three times and dried at 70 °C for 12 h.

1.1.3. Synthesis of Au/TiO₂

The Au/TiO₂ catalysts with 1.5 *wt.*% Au loading was prepared by a wet impregnation method. Briefly, TiO₂ supports (200 mg, Sigma-Aldrich, < 100 nm, 99.99% trace metals basis) were dispersed in an ethanol solution with 0.015 mmol HAuCl₄. Then, the ethanol solution was evaporated at 80 °C under stirring. Finally, the Au/TiO₂ catalysts were reduced by 5% H₂/Ar at 300 °C for 2 h.

1.1.4. Synthesis of Mn₂O₃

 Mn_2O_3 was obtained by calcining $Mn(NO_3)_2 \cdot 4H_2O$ at 500 °C for 2 h.

1.1.5. Synthesis of NS-MnOOH

Typically, the solution was obtained by mixing 2 mmol of manganese (II) nitrate tetrahydrate $(Mn(NO_3)_2 \cdot 4H_2O)$ and 10 mmol of ammonium fluoride (NH_4F) in 40 ml ultra-pure water for 1 h in the magnetic stirrer. Then, the solution was placed in Teflon-lined stainless-steel autoclaves and treated

at 120 °C for 12 h. At the end of the experimental period, the solution was cooled down to room temperature and thoroughly washed with ultrapure water and ethanol several times, then dried at 60 °C for 12 h in an oven (*J. Mater. Sci.-Mater. El.*, 2019, **30**, 8201-8209).

1.2. Characterization of catalysts

TEM characterizations were performed on a Hitachi HT-7700 electron microscope with an accelerating voltage of 120 kV. HRTEM images were collected on a JEOL-2100F instrument with an accelerating voltage of 200 kV. XRD patterns were obtained using a Rigaku Powder X-ray diffractometer with Cu K_{α} radiation. Specific surface areas were measured by using ASAP 2020 HD 88 (Micromeritics Co.) apparatus by a nitrogen physisorption method based on the Brunauer-Emmett-Teller (BET) method. XPS profiles were acquired from a Thermo Electron Model K-Alpha with Al K α as the excitation source. FT-IR analysis was taken on a Thermo Scientific Nicolet 6700 Fourier transform infrared spectroscopy, and all of the samples were mixed with KBr and pressed to a thin plate for measurements.

1.3. Catalytic reactions

For a typical catalytic reaction, 0.5 mmol of aniline and 20 mg of catalysts were mixed in 2.0 mL of toluene in a 10 mL glass reactor. Then, the reactor was transferred into a stainless-steel autoclave equipped with the pressure and temperature control system. The catalytic reactions were performed at given temperatures and 0.5 MPa O₂ under vigorous stirring (650 rpm). After reaction, the mixture was cooled and the catalysts were removed by hot filtration. The products were analyzed by gas chromatography (GC) and gas chromatography mass spectrometry (GC-MS).



Figure S1. (a) Outer diameter and (b) inner diameter distributions of NT-MnOOH.



Figure S2. EDS mapping images of (a) NT-MnOOH and (b) NW-MnOOH catalysts.



Figure S3. Diameter distribution of NW-MnOOH.



Figure S4. (a) XRD pattern and (b) TEM image of the Mn_2O_3 catalyst, (c) XRD pattern and (d) TEM image of the MnOOH nanosheets (NS-MnOOH).



Figure S5. TEM image of the Au/TiO₂ catalysts. The Au loading was 1.5 *wt.*%.



Figure S6. Nitrogen adsorption isotherms of (a) NT-MnOOH and (b) NW-MnOOH. (c) The surface areas of NT-MnOOH and MW-MnOOH.



Figure S7. Catalytic behavior of NT-MnOOH for the oxidative coupling of aniline at various reaction temperatures. Reaction conditions: aniline (0.5 mmol), catalyst (20 mg), toluene (2 mL) and 0.5 MPa O_2 .



Figure S8. Catalytic behavior of NW-MnOOH for oxidative coupling of aniline at various reaction temperatures. **Reaction conditions:** aniline (0.5 mmol), catalyst (20 mg), toluene (2 mL) and 0.5 MPa O₂.



Figure S9. Aniline conversions as a function of reaction time at various temperatures and plots of $\ln k$ as a function of (1/T) for NT-MnOOH catalyst, derived from aniline reaction rates *vs.* reaction time.



Figure S10. Aniline conversions as a function of reaction time at various temperatures and plots of $\ln k$ as a function of (1/T) for NW-MnOOH catalyst, derived from aniline reaction rates *vs.* reaction time.



Figure S11. XRD pattern and TEM image of the used NT-MnOOH catalyst.



Figure S12. 2,6-di-*tert*-butyl-4-methylphenol as trapping agent to stop the NT-MnOOH catalyzed oxidative coupling of aniline. **Reaction conditions:** aniline (0.5 mmol), 2,6-di-*tert*-butyl-4-methylphenol (0.6 mmol), catalyst (20 mg), toluene (2 mL), 60 °C and 0.5 MPa O₂.



Figure S13. The GC and GC-MS results of the oxidative coupling of aniline in the presence of 2,6-di-*tert*-butyl-4-methylphenol catalyzed by NT-MnOOH. **Reaction conditions**: aniline (0.5 mmol), 2,6-di-tert-butyl-4-methylphenol (0.6 mmol), NT-MnOOH (20 mg), toluene (2 mL), 60 $^{\circ}$ C, 0.5 MPa O₂ and 2 h.



Figure S14. XRD pattern and TEM image of the NT-MnOOH-T (T= 8, 9, 10, 11, 12) catalyst.



Figure S15. XPS spectra of (a) Mn 2p3/2 and (b) Mn 3s for various NT-MnOOH-T catalysts. (c) AOS of various NT-MnOOH catalysts. (d) The difference between Mn^{AOS} and Mn³⁺ of various MT-MnOOH catalysts.



Figure S16. (a) XPS analysis of O 1s for various NT-MnOOH catalysts. (b) the O²⁻/OH⁻ ration of various NT-MnOOH catalysts.

Catalyst	Temp.	O ₂ (bar)	Time (h)	Conv	Sel.	Ref.		
1.5wt Au/TiO ₂	100	5 bar O ₂	44	100	98	science., 2008 , <i>322</i> , 1611 –1664.		
Mn ₂ O ₃	110	Air	12	>99	>99	Angew. Chem., 2016 , <i>128</i> , 2211 –2215.		
1.5wtAu–TiO ₂	100	5 bar O₂	27	100	98	Nat. Protoc., 2010 , <i>5</i> , 429-438.		
RuO _{2/} Cu ₂ O	85	Air	24	94		ACS Sustainable Chem. Eng., 2018 , 6, 11345–11352.		
0.5% Au/CeO ₂	100	5 bar O_2	10	100	93	Catal. Lett., 2010 , <i>134</i> , 204-209.		
OMS-2	160	8 bar O ₂	24	95	99	Catal. Sci. Technol., 2016 , 6, 1940-1945.		
Ru/Al ₂ O ₃	100	1 bar O ₂	3	36		Angew. Chem. Int. Ed., 2003 , 42, 1480-1483.		
Cu-BTC MOF	80	O ₂	12	80		New J. Chem., 2020 , 44, 5972-5979.		
Aquivion@SiO ₂	40	H ₂ O ₂	24	98	91	Green Chem., 2018 , <i>20</i> , 382-386.		
Ag and KOH as additive	R.T.	1 bar Air	24	100	97	ACS Catal., 2013 , <i>3</i> , 478–486.		
BiVO ₄ /g-C ₃ N ₄	27	O ₂	16	20.5	95	ACS Sustainable Chem. Eng., 2017 , 5, 2562–2577.		
g-C ₃ N ₄ /BiOBr	28	O ₂	4	5.4	100	Chem. Eng. J., 2020 , <i>394</i> , 124934.		
lr(dF-CF ₃ -ppy) ₂ (dtbpy)+	24	air	24	55	100	J. Am. Chem. Soc., 2021 , 143, 2938-2943.		

Table S1. Summary of the catalytic performance of oxidative coupling of anilines into aromatic azo compounds.

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Entry	Solvent	Catalyst (mg)	Pressure (O ₂)	Time (h)	Conv. (%)	Sel. (%)
1	acetonitrile	20	1 bar	12	13.2	>99.9
2	DMSO	20	1 bar	12	0	-
3	DMF	20	1 bar	12	0	-
4	1.4-dioxane	20	1 bar	12	3.14	>99.9
5	THF	20	1 bar	12	9.6	>99.9
6	toluene	20	1 bar	12	23.3	>99.9
7	toluene	5	1 bar	12	4.9	>99.9
8	toluene	10	1 bar	12	10.9	>99.9
9	toluene	15	1 bar	12	15.7	>99.9
10	toluene	30	1 bar	12	32.5	>99.9
11	toluene	20	5 bar	12	38.8	>99.9
12	toluene	20	10 bar	12	45.6	>99.9
13	toluene	0	5 bar	12	0	-
14 ^a	toluene	20 ^a	5 bar	12	0	-

Table S2. Optimization of reaction conditions for the oxidative coupling of aniline to aromatic azoxy compounds*

* Reaction conditions: aniline (0.5 mmol), NT-MnOOH (20 mg), toluene (2 mL), 0.5 MPa O₂.

^a Catalyzed by Au/TiO₂ with Au loading of 1.5 wt.%.

The MS results of various substrates in Table 1.











Entry 4



Entry 5



Entry 6







Entry 8

