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Recent progresses in the synthesis of MnO₂ nanowire and its application in environmental catalysis

Huikang Song,†^a Leilei Xu, †* Mindong Chen,* Yan Cui, Cai-e Wu, Jian Qiu, Liang Xu, Ge Cheng and Xun Hu

Nanostructured MnO₂ with various morphologies exhibits excellent performance in environmental catalysis owing to its large specific surface area, low density, and adjustable chemical properties. The onedimensional MnO₂ nanowire has been proved to be the dominant morphology among various nanostructures, such as nanorods, nanofibers, nanoflowers, etc. The syntheses and applications of MnO₂-based nanowires also have become a research hotspot in environmental catalytic materials over the last two decades. With the continuous deepening of the research, the control of morphology and crystal facet exposure in the synthesis of MnO2 nanowire materials have gradually matured, and the catalytic performance also has been greatly improved. Differences in the crystalline phase structure, preferably exposed crystal facets, and even the length of the MnO2 nanowires will evidently affect the final catalytic performances. Besides, the modifications by doping or loading will also significantly affect their catalytic performances. This review carefully summarizes the synthesis strategies of MnO₂ nanowires developed in recent years as well as the influences of the phase structure, crystal facet, morphology, dopant, and loading amount on the catalytic performance. Besides, the cutting-edge applications of MnO2 nanowires in the field of environmental catalysis, such as CO oxidation, the removal of VOCs, denitrification, etc., have been also summarized. The application of MnO2 nanowire in environmental catalysis is still in the early exploratory stage. The gigantic gap between theoretical investigation and industrial application is still a great challenge. Compared with noble metal based traditional environmental catalytic materials, the lower cost of MnO2 has injected new momentum and promising potential into this research field.

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1. Introduction

The worldwide emissions of atmospheric pollutants, such as CO and volatile organic compounds (VOCs), have greatly increased year by year with the rapid development of the global economy. For example, CO is generally regarded as a flammable, explosive, and toxic air pollutant, which is extremely harmful to human health and the living environment. Besides, it is also a weak direct greenhouse gas and has an

important indirect effect on global warming. 7-10 Generally, CO is mainly derived from the incomplete combustion of fuels. 11,12 As for the VOCs, they commonly include formaldehyde, benzene, toluene, xylene, etc.2 They can enter into the human body through breathing and skin permeation, causing discomfort to the body and even inducing cancer. Besides, VOCs are also considered as important precursors of high concentrations of PM_{2.5} and O₃ in the atmosphere. Therefore, it is greatly necessary to develop efficient technologies to control the emissions of CO, VOCs, and other atmospheric pollutants. The current technologies mainly include adsorption, separation, biodegradation, catalytic combustion, plasma coordinated catalysis, photocatalysis, etc. Among these strategies, the catalytic oxidation or combustion has attracted increasing attention due to the advantages of high purification efficiency, low reaction temperature, and low cost. Therefore, designing and developing the catalysts with advanced performances are the key solutions to the catalytic oxidation of these air pollutants.

Noble metals (Au,^{13,14} Pt,¹⁵⁻¹⁷ Pd,¹⁸ and Rh¹⁹) supported on particular metal oxides (CeO₂, Ce_xZr_{1-x}O₂ and Fe₂O₃) with excellent oxygen storage capacities usually perform high

^aCollaborative Innovation Centre of the Atmospheric Environment and Equipment Technology, School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, Nanjing, 210044, P. R. China. E-mail: leileixu88@gmail.com; chenmdnuist@163.com

^bCollege of Light Industry and Food Engineering, Nanjing Forestry University, Nanjing 210037. P. R. China

Jiangsu ShuangLiang Environmental Technology Co., Ltd, Jiangyin, 214400, P. R. China

^dSchool of Material Science and Engineering, University of Jinan, Jinan, 250022, P. R. China

[†] These authors contributed equally to this work.

catalytic activity toward CO oxidation. However, they are extremely restricted in wide and large-scale application due to the high price and scarcity. Thus, it is very important to design and explore the low-cost catalysts with identical catalytic performance to the noble metals. It was reported that various transition metal oxides (Co₃O₄,^{20,21} CuO,²² MnO₂,²³ and CeO₂ (ref. 24)) performed excellent catalytic activity for CO oxidation in the past decades. Among them, MnO₂ has been extensively investigated due to various advantages, such as low price, environmental friendliness, and relatively high activity.25,26 With the continuous studies on MnO2 based materials, it has been found that MnO2 based catalysts usually perform good oxidation activities for the VOCs, such as formaldehyde, toluene, benzene, dimethyl ether, etc. Besides, the catalytic oxidation ability of MnO₂ can be greatly improved through crystal facet exposure engineering and regulating the loading

Compared with the traditional bulk MnO₂, the nanostructured MnO2 materials usually perform better physiochemical characteristics, such as the higher specific area, lower density, and more adjustable chemical nature. Furthermore, various studies have shown that MnO2 with nanowire morphology usually perform high surface areas and strong metal-support interactions.²⁷⁻³¹ Therefore, the nanowire is the dominant morphology among the MnO2-based nanostructured materials. Compared with MnO2 nanorods, MnO2 nanowires commonly possesses much more adsorbed surface oxygen, greater reducibility, higher specific area, and lower Mn-O bond strength, accounting for the better catalytic performances in the catalytic combustion of dimethyl ether²⁷ and plasma catalytic oxidation of toluene.28 Saputra et al.29 found that MnO2 nanowire displayed much higher activity than the MnO2 nanorod and nanofiber counterparts in activating oxygen ketones to degrade phenol. In addition to this, compared with rod-shaped and tubular MnO₂, the MnO₂ nanowire as the support behaved stronger interaction with Ag and displayed the much higher reactivity of toluene oxidation.30 The α-MnO2 nanowire also displayed the best catalytic activity toward gaseous benzene oxidation among the MnO2-based nanomaterials with different morphologies (e.g., wire and rod-like α-MnO₂, β-MnO₂ microrods) even after decorating Co₃O₄ nanoparticles.³¹

In recent years, more and more advanced and important materials have been developed for the applications of MnO2based nanomaterials in the removal of environmental pollutants,32,33 biosensing,34 theranostic,35 especially in the field of electrochemistry.36-38 For example, Li et al.37,38 synthesized α-MnO₂ nanowires with outstanding circulation stability, demonstrated rate performance, and high specific capacitance for supercapacitor electrode. Therefore, the previous reviews of MnO2-based nanomaterials were mainly focused on their applications in electrochemistry.39-43 However, there were few reviews paid close attention to their environmental applications. Yang et al.44 systematically summarized the environmental applications of MnO2-based materials. But they did not specially highlight the unique advantages of MnO2-based nanowire materials, which have been considered as the basic assembly unit of two-dimensional or three-dimensional

structure complex/heterostructure materials of MnO₂ (ref. 45) and normally have higher catalytic activity compared with MnO2-based nanomaterials in other morphologies.27-30 Meanwhile, the previous discussions about MnO2-based nanowire materials were very scattered and their applications were mainly focused on the topic in the field of the electrochemistry. There has been few comprehensive reviews targeting the applications of MnO2-based nanowire materials in the field of environmental catalysis. A systematic overview of frontier scientific research on the modulation of MnO2-based nanowire materials for environmental catalysis application is urgent for the rational design and fabrication of high-efficiency MnO2-based nanowire materials. Therefore, this review comprehensively summarizes the synthesis methods of MnO2-based nanowires, such as hydrothermal, reflux, sol-gel, template method, etc., and analyses the effects of various influencing factors, such as the crystalline phase structure, crystal facet, morphology, doping, and loading, on the performances of catalytic oxidation of CO, VOCs, and other environmental pollutants. In addition, the latest research progresses of MnO₂-based nanowire materials in the field of environmental catalysis are also covered in this review. With the in-depth research on MnO2-based nanowire materials, their environmental applications have been greatly improved. However, there is still big gap between the theoretical study and practical application. Therefore, it is of great necessity to summarize the recent progresses for better understanding the real surface reaction mechanism, which will promise the future environmental application in the fields of catalytic oxidation, combustion, purification, and other related research fields.

2. Synthesis of MnO₂-based nanowires

There are various preparation methods of MnO₂ nanomaterials, such as the liquid phase precipitation method, ^{46,47} reflux method, ⁴⁸ electrodeposition method, ⁴⁹ hydrothermal method, ⁵⁰⁻⁵³ sol-gel method, ^{54,55} template method, ⁵⁶ thermal decomposition method, ⁵⁷ and so on. As a result, the phase structures and chemical characteristics of MnO₂ nanomaterials fabricated by different methods will be completely different. Similarly, the synthesis of MnO₂-based nanowires also mainly employs the hydrothermal method, reflux method, sol-gel, and template method. Herein, the synthesis method, reaction condition, morphology parameters, and structural properties of MnO₂-based nanowires have been summarized in Table 1.

2.1 Hydrothermal synthesis method

The hydrothermal synthesis of MnO_2 -based nanowires mainly involves oxidation–reduction reaction of MnO_4^- and/or Mn^{2+} or the phase transition of MnO_2 precursor. The hydrothermal method usually involves several key parameters, including the reagent amount, reaction time, hydrothermal temperature, pH, and so on. Therefore, the MnO_2 -based nanowires with different phase structures can be synthesized in a precisely controllable way by tuning these key parameters in the hydrothermal process.

Table 1 The preparation method, raw materials, synthesis parameter, and the resultant structural properties of the MnO_2 -based nanowires

MnO ₂ nanowire	Preparation method	Raw materials	Synthesis temperature (°C)	Synthesis time (h)	Length	Diameter (nm)	$\begin{array}{c} \text{BET} \\ \left(\text{m}^2 \text{ g}^{-1}\right) \end{array}$	Reference
α-MnO ₂	Hydrothermal method	MnSO ₄ ·H ₂ O, KMnO ₄	150	12	2.5 μm	20-40	61.0	82
	Hydrothermal method	KMnO ₄ , NH ₄ Cl	200	48	Several µm	100-200	53.1	61
	Hydrothermal	$MnSO_4 \cdot H_2O$,	140	12	0.4-5 μm	5-20	148.0	29
	method Hydrothermal method	$(NH_4)_2S_2O_8$ δ -MnO ₂ , H_2SO_4	100	24	250–500 nm	30-60	93.1	27
	Hydrothermal method	KMnO ₄ , CH ₃ COOH	140	12	6–10 μm	30-60	39.9	83
	Reflux method	δ-MnO ₂ nanosheets	80-90	90-120	>10 µm	20-30	53.2	58
	Sol–gel template method	AAO template, Mn (CH ₃ COO) ₂ , citric acid	400	12	500–700 nm	70	_	54
β-MnO ₂	Hydrothermal method	$MnSO_4 \cdot H_2O$, $(NH_4)_2S_2O_8$	140	12	1.5–2.5 μm	60–100	55.7	84
	Hydrothermal method	Mn $(NO_3)_2$, O_3	200	8	2–5 μm	6–12	73.5	58
$\gamma\text{-MnO}_2$	Hydrothermal	$MnSO_4 \cdot H_2O$,	90	24	_	_	_	85
$\delta\text{-MnO}_2$	method Hydrothermal method	$(NH_4)_2S_2O_8$ $MnSO_4 \cdot H_2O$, $KMnO_4$	240	24	_	_	_	
α-MnO ₂ -100	Hydrothermal method	$\begin{array}{l} MnSO_4 \cdot H_2O, \\ (NH_4)_2S_2O_8, \ (NH_4)_2SO_4, \\ KNO_3 \end{array}$	120	20	Several μm	15-20	87.9	86
α-MnO ₂ -110	Hydrothermal method	$KMnO_4$, $(NH_4)_2SO_4$	180	24	_	45-50	119.5	
	Hydrothermal method	$KMnO_4$, $(NH_4)_2C_2O_4 \cdot H_2O$	180	24	100–500 nm	10-50	_	87
α -MnO ₂ -210	Hydrothermal method	MnCO ₃ , HNO ₃ , (NH ₄) ₂ S ₂ O ₈ , H ₂ SO4	140	2	100–500 nm	10-50	_	
α-MnO ₂ -310	Hydrothermal method	$KMnO_4$, $(NH_4)_2SO_4$	180	24	100–500 nm	10-50	_	
	Hydrothermal method	$KMnO_4$, $(NH_4)_2C_2O_4$	180	24	Several µm	15-20	135.3	86

DeGuzman et al.50 pointed out that pH and temperature could affect the final phase structure of MnO2 in the synthesis of fibrous α-MnO2 nanomaterials and α-MnO2 would transit into β-MnO₂ when the temperature was kept above 120 °C. However, Wang et al. 51 found that the effects of pH and temperature were not significant. In their study, 1D MnO2 nanomaterials with different phase structures could be obtained in a wide temperature range (100-180 °C) just by varying the molar ratio of raw reactants (KMnO₄ and MnSO₄) without adjusting the pH (~ 2.5) of the system. Besides, the type of the raw reactants greatly determines the hydrothermal reaction temperature of preparing the α-MnO₂ nanowire. For example, the optimal hydrothermal temperature was located between 120 °C and 160 °C when using KMnO₄ and MnSO₄·H₂O as raw materials;58-60 whereas, the optimal hydrothermal temperature was 200 °C when using KMnO₄ and NH₄Cl as the precursors. ⁶¹⁻⁶³ The effect of pH on the crystalline phase structure of the final product was also largely derived from the ion concentration as the tunnels of different MnO2 crystal forms have different sizes and need different amounts of cations to stabilize.64 Zhang et al. 53 showed that the phase structure of MnO2 and the aspect ratio of the final product were greatly depended on the concentration of ions in the reaction system, especially K⁺. Because the high concentration of K+ could be used as the effective template, which was more conducive to the synthesis of α-MnO₂ nanowire.⁵³ Wang et al.⁵¹ believed that the layer structure of δ -MnO₂ tended to curl under the high temperature and pressure, which was considered as the determinant step for the formation of 1D nanostructures of MnO₂. Zhang et al.⁵³ also indicated that prolongating hydrothermal time could drive the self-assembly of α-MnO₂ into bundles and then transform into β-MnO₂. Therefore, the possible synthesis route of MnO₂-based nanostructures was described in Fig. 1. First, the MnO_r units appear in the solution and the δ-MnO₂ with the layer structure is then formed through a series of condensation reactions. δ -MnO₂ tends to curl under high temperature and high pressure. When K⁺ concentration is high, α-MnO₂ can be formed; otherwise, β-MnO₂ can be formed. With the prolonging of hydrothermal time, the $[2 \times 2]$ tunnel structure of α -MnO₂ directly collapses into the $[1 \times 1]$ tunnel structure of β -MnO₂.⁵³ Wei

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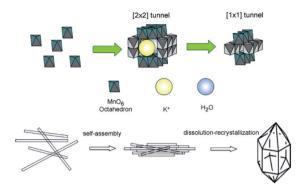


Fig. 1 Schematic illustration of the self-assembly of α-MnO₂ nanowires into bundles and their subsequent phase transformation to β -MnO₂ microcrystals under prolonged hydrothermal conditions. Reproduced by Zhang $et~al.^{53}$ with permission from Elsevier.

et al. 52 studied the hydrothermal synthesis of MnO2-based nanowires through the phase transition of granular MnO2 precursor. They synthesized α -MnO2 and β -MnO2 single crystal nanowires by the hydrothermal treatment of γ -MnO2 at different temperatures. This method not employing catalysts or templates could be easily reproduced. Therefore, the hydrothermal synthesis of different crystal types of MnO2 nanowires with potential application prospects in large-scale could be realized.

Generally, the hydrothermal method of preparing MnO₂-based nanowire has various advantages, such as high product purity, excellent dispersion, good crystallinity, uniform morphology, *etc*. Besides, the preparation conditions are simple and the fabrication time is short. Therefore, the hydrothermal method has been widely used for the synthesis of MnO₂-based nanowires. However, the hydrothermal method is usually limited by the capacity of the reaction system, so it is not suitable for the large-scale industrial production. Furthermore, the tightness of the reaction system will bring safety hazards.⁶⁵

2.2 Reflux method

The reflux is a kind of wet chemical synthesis method that does not require high-temperature calcination, and directly synthesizes nanomaterials with uniform particle size and high activity. The reflux method is suitable for the large-scale synthesis of MnO2 nanowires owing to various advantages, such as simple operation and mild reaction conditions. Kijima et al.66 synthesized MnO₂ with three different phase structures (α -, β -, and γ -) by the acid digestion of Mn₂O₃ under reflux conditions. The type of polymorph of MnO₂ products was strongly dependent on the reaction temperature, type of acid used, and the concentration. When H₂SO₄ was used as the acid, the α-MnO₂ was inclined to form at higher H₂SO₄ concentrations and lower reaction temperatures. In contrast, the β-MnO₂ was obtained at lower H₂SO₄ concentrations and higher reaction temperatures. The γ -MnO₂ were formed at intermediate conditions. When HNO₃ was used as the acid, only the β-MnO₂ and γ-MnO₂ could be formed. The α-MnO₂ could not be obtained in the HNO₃ solution. Compared with γ -MnO₂, the β -MnO₂ formation

usually demanded higher reaction temperatures (>80 °C) and higher concentrations of HNO₃ (>10 mol L⁻¹).⁶⁶ Chen et al.⁶⁷ synthesized transition metal doped α-MnO₂ nanofibers by the reflux method. Compared to the pristine MnO2, metal cation doped MnO2 materials had slightly higher surface areas and pore volumes, especially when the dopant content was relatively high. Jin et al.68 synthesized γ-MnO2 homogeneous nanofiber with the length of \sim 1 µm and the diameter of 50 nm by refluxing and used it as the catalyst for catalysing the atmospheric oxidation of toluene with molecular oxygen. Sinha et al.65 prepared δ-MnO₂ nanosheets by the reflux method and further deepened the morphological evolution and shape transformation into ultra-long α-MnO2 nanowires with extremely high purity by reflux. The length of the nanowire was observed to exceed 10 µm. The detailed preparation process and SEM results are shown in the Fig. 2. The reflux method also has the advantage of low chemical cost and avoids using autoclaves under harsh hydrothermal reaction conditions. As a result, the high-quality α-MnO₂ nanowires could be generated without using catalysts and stencils. The reflux method provides a promising preparation method of α-MnO₂ nanowires in large scale.65 May et al.69 synthesized α-MnO2-based nanowires and further studied the effect of doping methods on lowtemperature CO oxidation of CuO/α-MnO2 catalysts based on the nitric acid reflux method of Uematsu et al.70

2.3 Sol-gel method

As for the sol-gel method, it employs the metal alkoxides or inorganic salts as precursors to achieve gelation through continuous hydrolysis and polycondensation processes. Then, the gel experiences the heat, and other subsequent treatments to obtain the final target product. The sol-gel synthesis of nanostructured MnO₂ commonly includes various combinations of hydrated metal cations, such as manganese acetate (MnAc₂) and citric acid,⁷¹ MnAc₂ and n-propyl alcohol,⁵⁴ tetrabutylammonium permanganate and methanol,⁷² and KMnO₄

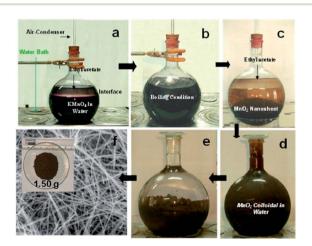


Fig. 2 Preparation of gram level α -MnO₂ nanowires from aqueous KMnO₄/ethyl acetate biphasic system and their different stages (a-f) in digital/FESEM images. Reproduced by Sinha *et al.*⁶⁵ with permission from ACS.

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and fumaric acid (C₄H₄O₄).^{73,74} The structures of the obtained MnO2 are strongly depended on the molar ratio between the KMnO₄ and the organic reducing agents.⁷⁵ For example, the 3:1 reactant ratio of KMnO₄ to glucose favoured the cryptomelane (2 \times 2 tunnel) synthesis, while the 5 : 1 ratio generated the layered birnessite-type material.⁷² Hastuti et al.⁷⁴ synthesized irregular spherical α-MnO₂ particles by the sol-gel method and discovered that transition metal (Fe³⁺, Cu²⁺) doping did not affect the phase structure but only changed the lattice parameters and morphology of the final product. Hashem et al.76 prepared the α-MnO₂ materials by redox reaction of KMnO₄ and ascorbic acid using the sol-gel method. The morphology of the final sol-gel samples were long needles with uniform diameter of \sim 15 nm and average length of \sim 0.8 μ m, and further aggregated to urchin-like balls. Hashemzadeh et al. 71 prepared y-MnO₂ polymorph using the manganese acetate and citric acid as the raw reagents in the sol-gel way. The obtained γ-MnO₂ polymorph was composed of particles with surface covered with needle-like nanorods. The researches have demonstrated that the sol-gel method could prepare 1D nanostructure MnO₂ nanowire with different morphologies. Ghorbani et al.77 successfully synthesized MnO2 nanowires with 45 nm in diameter using simple precursors, such as KMnO₄ and NaNO₃, by sol-gel method. They found that the optimal annealing temperature for achieving crystalline structure and nanowire morphology was 600 °C. Chin et al.78 successfully prepared MnO2 nanowires via the self-assembly of MnO2 nanoparticles using the sol-gel method with KMnO₄ and Mn(ClO₄)₂ as the precursors. The microstructure and morphology of sol-gel derived MnO2 nanowire were affected by the synthesis conditions and post synthesis heat treatment. Acidic pH value (pH 5.7) and calcination temperature at 300 °C were effective on achieving nanowire morphology and high surface area. Liu et al.79 synthesized wire-like ion sieve MnO2 · 0.5H2O with about 50-200 nm in diameter and 0.5-2 µm in length using the sol-gel method. The ion sieve MnO2·0.5H2O nanowire had excellent adsorption performance for lithium extraction in seawater system and had a good application prospect. Furthermore, the combination of sol-gel and template has been considered as better way to synthesize highly-ordered MnO2-based

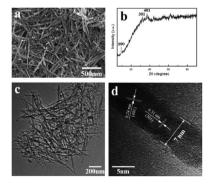


Fig. 3 (a) SEM image, (b) XRD pattern, (c) and (d) TEM images of MnO_2 nanowire prepared by sol–gel approach. Reproduced by Tang *et al.*⁵⁵ with permission from Elsevier.

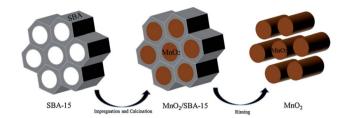


Fig. 4 Schematic representation of the preparation of MnO_2 by SBA-15 template. Reproduced by Zhang *et al.*⁸⁰ with permission from Elsevier.

nanowires than the sol–gel itself. 54,55 As shown in Fig. 3, Tang *et al.* 55 used CTAB as the surfactant to obtain highly dispersed ultrafine MnO₂ nanowires with the diameter of only 7 nm by the template directed sol–gel template method.

2.4 Template method

The template method has been considered as a common method for preparing nanomaterials by employing various structure directing agents or templates in recent years. Nanomaterials with ordered structures are generated through the guidance of the template in the form of self-assembly by using the organic molecules as template agents. For example, Wang $et\ al.^{54}$ successfully prepared $\alpha\text{-MnO}_2$ nanowire with the diameter of about 70 nm and the length between 500 nm and 700 nm using the sol–gel template method. The length and diameter of the nanowires greatly depended on the pore size and thickness of the employed AAO template. Gu $et\ al.^{56}$ used mesoporous silica SBA-15 as the hard template to prepare highly ordered array of mesoporous $\beta\text{-MnO}_2$ nanowires by the nano-casting method. Fig. 4 shows the schematic representation of the preparation of MnO₂ by using the SBA-15 as the template. So

The morphology of materials synthesized by the template method can be tunable by the choice of the template. However, the use of templates obviously increases the production cost. Therefore, reducing the costs of the templates is still an important concerned issue. Wang et al. ⁸¹ fabricated hierarchical MnO₂ microfibers by using cotton as the template and KMnO₄ as the precursor. In comparison with other templates, biological materials are "green" and easy to obtain, and the morphology of cotton fiber is more uniform than other kinds of plant fibers. This green, sustainable, and low-cost biotemplating method can be extended to the synthesis of MnO₂-based nanowires and other metal oxide materials in the view of economical concern.

3. The factors affecting the catalytic performances of MnO₂ nanowires

3.1 Phase structure

The [MnO₆] octahedral unit is the basic building block for crystalline-phase MnO₂ materials. As shown in Fig. 5, when [MnO₆] octahedral units are linked in different ways, the MnO₂ can form a variety of polymorphs, such as α -, β -, γ - and δ - MnO₂.*8-90 Studies have found that the phase structure can

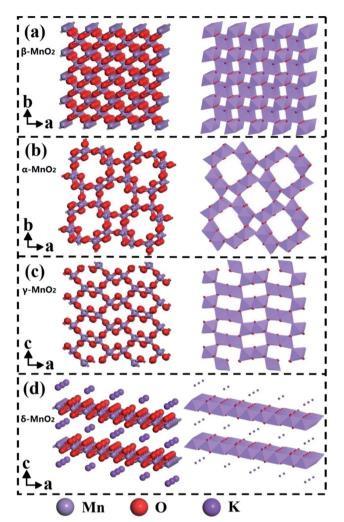


Fig. 5 Ball-stick and polyhedron representations of (a) β -, (b) α -, (c) γ - and (d) δ -MnO₂. Reproduced by Li *et al.*⁹¹ with permission from Elsevier.

significantly affect the catalytic activity of MnO_2 , and both α - MnO_2 and δ - MnO_2 are the dominant phase structures of MnO_2 -based catalytic nanomaterials. 91-94

Specifically, α -MnO $_2$ occupies more space than β -, γ -, and δ -MnO $_2$ due to the double tunnel structure of $[2\times2]$ and $[1\times1]$. As a result, it obtains more adsorption sites for the reactants (such as CO and VOCs) than other phases. At the same time, the existence of surface open pore structure can also increase the surface area of α -MnO $_2$ nanowires, thereby providing abundant oxygen adsorption sites for the reactants. In addition, α -MnO $_2$ also has the weakest Mn–O bond strength among these crystalline phase structures, which could provide the lattice and absorbed oxygen during the oxidation reaction. Therefore, α -MnO $_2$ performs much better activity than other phase structures in catalytic reactions, such as CO oxidation, α -O α -0 catalytic degradation, plasma oxidation of toluene, and degradation of phenol by activating oxyketone.

 $\delta\text{-MnO}_2$ is composed of [MnO $_6$] octahedrons shared by the double layer edges. The special layer structure makes it easy for

toluene molecule to absorb on the surface of δ -MnO $_2$ and thereby behaves excellent activity in the catalytic oxidation of toluene. As the comparison, the α -MnO $_2$ performs weaker toluene oxidation activity due to the lower content of Mn $^{4+}$ and lattice oxygen. Besides, δ -MnO $_2$ has also been proved to be the best crystalline phase structure for low-temperature catalytic oxidation of formaldehyde. A

β-MnO $_2$ with [1 \times 1] tunnels have the most stable redox ability among these four phase structures. Besides, the surface area of β-MnO $_2$ nanowire materials is usually the smallest among the four phase structures, which will greatly hinder the adsorption and activation of the reactants and oxygen. As a result, it usually performs the lowest activity in the catalytic oxidation of CO and VOCs. The [2 \times 1] and [1 \times 1] tunnel structures of γ -MnO $_2$ have relatively mediocre catalytic activity in the oxidation of CO and VOCs.

3.2 Crystal facet

Studies have shown that the catalytic activities toward specific substances can be significantly improved by synthesizing nanomaterials with a high proportion of exposure specific crystal facets.^{95–97} Recently, more and more studies have paid attention to the influence of specific crystal facets on their catalytic effects, such as TiO₂, ⁹⁵ Fe₂O₃, ⁹⁶ CeO₂ (ref. 97) and Co₃O₄, ²⁰ because they are closely related with the final catalytic performances. Meanwhile, the great progresses have been made in the application of specific crystal facet of MnO₂-based nanowires to the catalytic oxidation of VOCs, such as formal-dehyde, ⁸⁶ methylmercury ⁹³ and toluene, ⁸⁷ etc.

Theoretically, the reactivity and activity of crystal faces are proportional to their surface energy. Therefore, the crystal facets with higher surface energies are usually more reactive in heterogeneous reactions.98 Many studies have been carried out on the α-MnO₂ nanowires because α-MnO₂ has highest activity among the four phase structures of MnO₂-based nanowires. The characteristic crystal facets of α-MnO₂ generally include (310), (100), (110), and (210). Among them, (310) crystal facet possesses the highest surface energy, which is beneficial to the formation of oxygen vacancy. Thereby, the adsorption and activation of O2, H2O (ref. 86) and O3,93 etc., could be promoted. As a result, (310) crystal facet performs obviously better activities on the oxidation of formaldehyde and the ozonation of methylmercury than (100) and (110) counterparts (see Fig. 6). Rong et al.86 reported that the 310-α-MnO2 could completely convert 100 ppm formaldehyde to CO₂ at 60 °C, which was even better than some silver-based catalysts. 99,100 As shown in Fig. 7, the (310) facets with high surface energy could not only facilitate adsorption/activation of O2 and H2O but also be beneficial to the generation of oxygen vacancies, which resulted in significant enhancement of HCHO oxidation activity. He et al.93 reported that the 310-α-MnO₂ could completely remove 70 ppm of methyl mercaptan within 20 minutes at room temperature. However, crystal planes with higher surface energy usually disappear in most crystals with the fast growth and the thermodynamically stable crystal planes would preferentially dominate the surface to minimize the total surface energy of the

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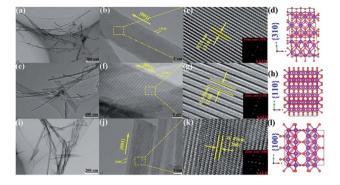


Fig. 6 TEM and HRTEM images of (a-c) α -MnO₂-310, (e-g) α -MnO₂-110, and (i-k) α -MnO₂-100. Atomic structure of the (d) {310}, (h) {110}, and (I) $\{100\}$ surface of α -MnO₂. Small (red) spheres are oxygen and large (purple) are manganese. Reproduced by Rong et al.86 with permission from ACS.

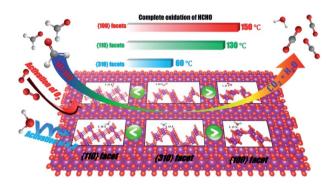


Fig. 7 α -MnO₂ nanowires with (100), (110) and (310) facets for HCHO oxidation. Reproduced by Rong et al.86 with permission from ACS.

crystal.86 Meanwhile, Huang et al.87 found that (210) crystal plane with the lower surface activation energy (24.75 kJ mol⁻¹) showed better catalysis activity and stability for toluene than (110) and (310) crystal plane. The lower surface activation energy accelerated the activation and oxidation of toluene. The alternating arrangement of Mn-O atoms in the electronic structure also speeds up the oxidation and desorption of intermediate products, thus exhibiting excellent activity.

All in all, the specific VOCs oxidation reaction mechanism on the MnO2-based nanowires is the key to improving the oxidation ability of MnO2-based nanowire catalyst to VOCs through crystal facet engineering. It is also greatly necessary to strengthen the research on the mechanism of catalytic oxidation of VOCs because of the specific advantages of each crystal facet of MnO2-based nanowires.

3.3 Morphology

As well known, the physiochemical properties of MnO2 with different morphologies are often different. 101,102 The common one-dimensional structure of MnO2 includes nanorods, nanotubes and nanowires. Among these morphologies, the MnO2 nanowires occupies an important place. Because onedimensional nanowires can be used as the basic assembly unit of two-dimensional or three-dimensional structure

materials.45 Furthermore, the composite materials with novel structures and properties can be facilely prepared on the basis of them.

One of the basic parameters greatly affecting the performance of nanowires is the length or aspect ratio. For example, the photocatalytic performance of W₁₈O₄₉ nanowires is greatly affected by its aspect ratio; 103 the dielectric properties of BaTiO3 nanowires also have close relationship with its length.¹⁰⁴ Therefore, the performance of the nanowire can be tuned by controlling the length or aspect ratio. Liao et al. 105 investigated the influence of the length of α-MnO₂ nanowires on the catalytic combustion performance of dimethyl ether. The results revealed that the length of the nanowires would affect the redox property of α-MnO₂ and the final catalytic combustion performance of dimethyl ether. Among them, α-MnO₂ nanowires with medium length (4-8 µm) possessed the best catalytic performance with ignition temperature at 167 °C and the complete combustion temperature at 240 °C. The 20 h life test demonstrated that the sample behaved good stability without deactivation.105 Li et al.91 prepared three kinds of δ-MnO2 with different crystallinities and morphologies. The complete toluene conversion was achieved at 250-275 °C for δ-MnO₂ and the toluene conversion efficiency of δ-MnO₂ would be promoted with the decrease of crystallinity degree and particle size. Although the effect of the crystallinity and morphology were not as significant as the phase structure, they indeed greatly affected the activity of MnO2 in the catalytic oxidation of toluene.

3.4 Metal loading and doping

The metal loading and doping are two common used modification methods when preparing catalyst. Both of them could significantly improve the catalytic activity of the MnO₂-based nanowire. The loading method could highly and uniformly disperse metal or metal oxide on the surface of catalytic support and the catalysts with higher activities could be achieved due to the formed strong metal-support interactions. 106 The doping method is to replace a small portion of the second metal cations in the host metal oxide with different cations can greatly change the chemical bonding on the surface of the host metal oxide, thereby improving its catalytic performance.107 The active site in such catalytic system could be either the oxygen atoms near the dopant or the dopant itself. As a result, the activity of MnO2based nanowire can be further improved by dispersing more active ingredients on its surface.

The studies related to the metal modification of MnO₂ usually starts with the loading of noble metals, such as Au and Ag. For example, Gu et al. 56 loaded Au nanoparticles on α-, β-MnO₂ nanowires and developed Au/MnO2 catalyst with extremely high activity and stability for CO oxidation at low temperature. The Au/ α-MnO₂ nanowire catalyst showed the CO conversion of around 37% at -90 °C. As the temperature increased, the CO conversion increased rapidly to 90% below $-60\,^{\circ}\text{C}$, and slowly reached 100% at around -34 °C. The low-temperature (-85 °C) CO oxidation rate over this catalyst (2.8 mol_{CO} h⁻¹ g_{Au}⁻¹) was almost 30 times higher than that of the Au/Mn₂O₃.¹⁰⁸ Qin et al.¹⁰⁹ investigated the

toluene oxidation activity over the α-MnO₂ nanowires supported catalysts with different Ag loading amounts, which greatly affected the toluene oxidation performance. As could be seen in Fig. 8, 4% Ag/MnO₂ catalyst performed the highest activity of the toluene oxidation and the lowest apparent activation energy (45.5) KJ mol⁻¹) among Ag/MnO₂ catalysts. They found that 4% loading of Ag could greatly facilitate the adsorption of toluene molecules and optimally increase the activation capacity of MnO₂ lattice oxygen between the interface of Ag and MnO2, thereby increasing the reaction rate and promoting deep oxidation between toluene and lattice oxygen. 109 Apart from the loading of noble metals, Sadeghinia et al.84 reported that the catalytic activity of CO oxidation could be enhanced by loading the α-MnO2 nanowires with different contents of CuO. The 30% CuO/α-MnO₂ catalyst could achieve the complete CO conversion at about 100 °C, which was nearly 100 °C lower than pristine α-MnO₂ nanowire. May et al. 69 further confirmed that the loading of CuO by the deposition precipitation (DP) method would make the onedimensional nanostructure of MnO2 with more excellent CO catalytic oxidation activity than the incipient wetness impregnation. Specifically, the most active 5CuO/MnO2 could achieve 80% CO conversion rate at 30 °C.

In view of the excellent performance of CuO loaded MnO₂-based nanowire catalysts, ⁸⁴ the researches gradually focused on the transition metals doped catalysts because of the low cost and abundant availability. Lambert *et al.*¹¹⁰ reported that the catalytic activities of α -MnO₂ nanowires doped with Cu and Ni

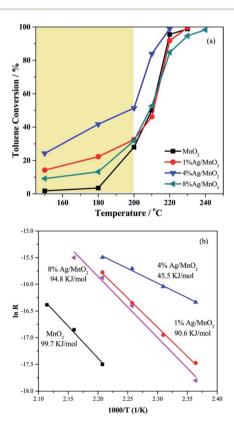


Fig. 8 (a) Catalytic performance of the catalysts for toluene oxidation; (b) Arrhenius plot of the reaction rate of the catalysts. Reproduced by Qin *et al.*¹⁰⁹ with permission from Elsevier.

were significantly better than that of the pristine α-MnO₂ nanowires. Gao et al. 61 investigated the effects of doping Fe, Co, Ni, and Cu transition metals on the catalytic performance CO oxidation of α-MnO2 nanowires. As shown in Fig. 9, the appropriate amount of transition metal doping would not apparently change the morphology, phase structure, and specific surface area of MnO2 nanowires. As could be observed in Fig. 10, the CO oxidation activities of the transition metal doped α-MnO2 nanowires were also significantly increased. Among them, Cu doped α-MnO₂ nanowires showed the best CO oxidation activity. The density functional theory calculations further revealed that doping Cu could more easily form oxygen vacancies in MnO₂ than doping Fe, Co, and Ni, which was the determinant of the CO oxidation reaction rate. Therefore, the Cu-doped nanowires performed the higher CO oxidation catalytic activity than those for noble-metal-free catalysts, such as Cu-substituted Co₃O₄, ¹¹¹ Cu-doped CeO₂, ^{112,113} CuO/Al₂O₃. ¹¹⁴ In addition, Jampaiah et al.62 also studied the MnO2 nanowires doped with two transition metals. Their results showed that the Cu and Co doped MnO₂ nanowires could greatly improve the soot oxidation activity and its T50 of soot conversion was as low as 279 °C. The advantage of two transition metals doped MnO₂ nanowires was that it enhanced the strong synergistic interaction between the transition metals. However, this study had shown that there was an upper limit for the amount of surface metal doping of MnO₂ nanowires. Because the original nanowire morphology would be damaged when the surface metal doping amount reached 20%.62

3.5 Interface effect

The interface effect derived from nanostructures plays an important role in enhancing the catalytic activity. It is widely

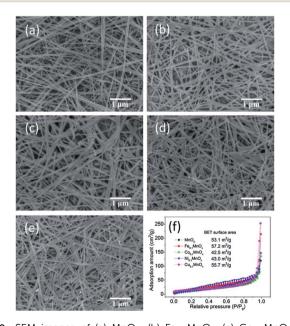


Fig. 9 SEM images of (a) MnO $_2$, (b) Fe $_{0.1}$ MnO $_x$, (c) Co $_{0.1}$ MnO $_x$, (d) Ni $_{0.1}$ MnO $_x$, and (e) Cu $_{0.1}$ MnO $_x$ nanowires and (f) N $_2$ adsorption–desorption isotherms. Reproduced by Gao *et al.*⁶¹ with permission from Elsevier.

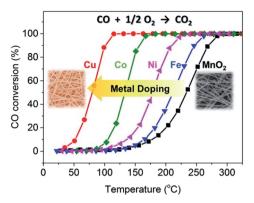


Fig. 10 CO oxidation activity tests of the MnO₂ and Fe-, Co-, Ni-, and Cu-doped MnO₂ catalysts. Reproduced by Gao *et al.*⁶¹ with permission from Elsevier.

believed that multi-component metal oxides with coupling interfaces often exhibit better catalytic activity than singlecomponent metal oxides. 115-119 For example, as regards the α-MnO₂@Co₃O₄ catalyst, the heterogeneous interface constructed by MnO2 nanowires and Co3O4 nanoparticles could not only enhance the redox pair of Mn4+/Mn3+ and Co2+/Co3+ but also strengthen the adsorption of oxygen on the surface and accelerate the fluidity of oxygen. As a result, the catalytic activities of α -MnO₂@Co₃O₄ toward the oxidation of benzene³¹ and toluene¹²⁰ were much better than that of pristine MnO₂ nanowires. The α -MnO2 nanowire@Co3O4 could reduce the T90 of benzene oxidation to 247 °C (see Fig. 11) and the T₉₀ of toluene conversion to 229 $^{\circ}$ C, which were 100 $^{\circ}$ C and 47 $^{\circ}$ C lower than that of the pure α-MnO₂ nanowire, respectively.31,120 Deng et al.121 successfully prepared the MnO2 nanowire@NiO nanosheet core-shell hybrid nanostructure by uniformly decorating NiO nanosheets on α-MnO₂ nanowires. The obtained catalyst could achieve the complete oxidation of benzene at 320 °C, which was 60 °C lower than the pure MnO₂ nanowire. Ma et al. 122 prepared MnO₂ (a TiO₂ by immobilizing crystalline anatase TiO_2 on the surface of α -MnO₂ nanowire. The as-prepared MnO₂@TiO₂ exhibited much higher maximum adsorption capacity (105.3 mg g^{-1}) of the

100 1D MnO₂@Co₃O₄ 247°C 345°C AT₉₀=98°C AT₉₀=98°C 1D MnO₂ 150 200 250 300 350 Temperature (°C)

Fig. 11 Benzene oxidation activity tests of the 1D MnO $_2$ @Co $_3$ O $_4$ and 1D MnO $_2$ catalysts. Reproduced by Tang *et al.*³¹ with permission from Elsevier.

radioactive element $U(v_I)$ than the pure MnO_2 (13.3 mg g^{-1}), illustrating that the performance of the surface-modified MnO_2 was greatly improved.

Homojunctions are junctions layer made of the same semiconductor materials.44 It has been revealed that the construction of homojunctions could enhance the adsorbing and catalytic performance of the MnO2 nanomaterials. 123,124 Zhou et al. 123 constructed α-MnO₂(a)δ-MnO₂ homojunction by loading layered δ-MnO₂ nanoflakes on the framework of α-MnO₂ nanotubes. The α-MnO₂@δ-MnO₂ homojunction integrated the exposed surfaces of the α -MnO₂ (100) surface and δ -MnO₂ (001) surface at the same time and displayed outstanding catalytic performance toward the oxidation of formaldehyde. The α-MnO₂ (100) surface was conducive to the adsorption and activation of oxygen molecules and the δ-MnO₂ (001) surface was favourable for the desorption of H₂O. The synergistic effect of the two surfaces significantly enhanced the catalytic activity for formaldehyde oxidation at room temperature. Huang et al. 124 synthesized the special two-phase structure MnO2 catalyst simultaneously with α -MnO₂ and β -MnO₂ (α -MnO₂: β -MnO₂ = 1:1). As a result, toluene could be completely oxidized over the α@β-MnO₂ two-phase catalyst at about 205 °C, which was lower than the pure α -MnO₂ (220 °C) and β -MnO₂ (260 °C). Compared with the single-phase MnO₂, the α@β-MnO₂ with two-phase structure generated more abundant active interface and oxygen vacancy, thus promising enhanced catalytic performances.

4. Application in catalytic oxidation

4.1 CO oxidation

CO is one of the most common atmospheric pollutants harmful to the health of human beings. Its capacity of binding to hemoglobin is about 210 times higher than O_2 . Therefore, the combination of CO and hemoglobin severely hinders the delivery of blood oxygen, which will cause the supply shortage of blood oxygen and further threaten the life safety. Given these drawbacks, the low-temperature catalytic oxidation of CO has been considered as one of the most important environmental catalysis

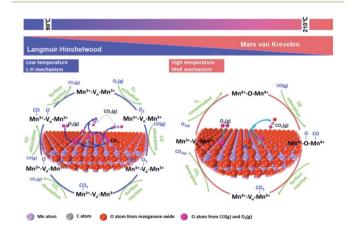


Fig. 12 Proposed reaction mechanism of CO oxidation on metal oxide. Reproduced by Tian *et al.*¹²⁶ with permission from Elsevier.

processes. As shown in Fig. 12, the proposed reaction mechanism of CO oxidation on manganese oxide catalyst commonly abides by Langmuir-Hinshelwood reaction mechanism (L-H mechanism) at low temperature (<90 °C) and Mars-van Krevelen reaction mechanism (MvK mechanism) at high temperatures (T > 190°C). 126 When the temperature is low (50-90 °C), gaseous O2 are captured by oxygen vacancies and the active oxygen species (O₂⁻ or O_2^{2-}) could be formed. Subsequently, the adsorbed CO (CO-Mn³⁺) tent reacts with active oxygen species to generate bidentate carbonate species, and then decompose into CO2. Finally, the dissociated O species could be restrained by oxygen vacancies and react with the adsorbed CO to form CO2 which follows the L-H mechanism. When the temperature is high ($T > 190 \,^{\circ}$ C), the surface lattice oxygen species can directly react with adsorbed CO to generate CO₂ and oxygen vacancies due to the activation of surface lattice oxygen species. Subsequently, the oxygen vacancy was refilled by gaseous O2 and the redox cycle is completed by following the MvK mechanism. The T₁₀, T₅₀, T₉₀, T₁₀₀ and BET of MnO₂-based nanowire materials on the catalytic oxidation of CO and some VOCs have been summarized in Table 2.

Previous studies found that the crystalline phase structure could significantly affect the CO catalytic activity of MnO2.26,92,127 Liang et al.26 synthesized four different crystalline MnO2 nanooxides. They found that the order of activity for catalytic oxidation of CO was $\alpha \approx \delta > \gamma > \beta$ -MnO₂. Because the tunnel structure of $[2 \times 2]$ and $[1 \times 1]$ of α -MnO₂ could occupy more space to obtain more CO adsorption sites; whereas, other crystalline MnO₂ only involved β -MnO₂ with $[1 \times 1]$ tunnel, γ -MnO₂ with $[2 \times 1]$ and $[1 \times 1]$ tunnels, and δ -MnO₂ composed of [MnO₆] octahedrons shared by the double-layer edges. Another reason accounting for the enhanced catalytic CO oxidation performance of α-MnO2 was that the elongated Mn-O bond length stemming from the distorted [MnO₆] units could benefit the cracking of the Mn-O bond, promoting CO oxidation. 26,127 As a result, α-MnO₂ could easily react with CO and thus further improved its catalytic performance.

Table 2 T_{10} , T_{50} , T_{90} , and T_{100} of MnO₂-based nanowire catalysts toward different catalytic substances

MnO ₂ based nanowire material	BET $(m^2 g^{-1})$	Catalytic substance	T ₁₀ (°C)	T ₅₀ (°C)	T ₉₀ (°C)	T ₁₀₀ (°C)	Reference
α-MnO ₂	31.3	CO	_	\sim 180	\sim 210	260	84
20% CuO/α-MnO $_2$	22.0		_	~75	\sim 100	150	
$Au/α-MnO_2$	40.0		_	-83	-60	-34	56
α -MnO $_2$	53.1		$\sim \! 180$	234	\sim 275	~ 300	61
$Fe_{0.1}MnO_x$	57.2		\sim 170	212	\sim 260	\sim 275	
$Co_{0.1}MnO_x$	42.5		\sim 110	133	~ 160	\sim 180	
$Ni_{0.1}MnO_x$	43.0		${\sim}140$	178	\sim 220	$\sim\!\!260$	
$Cu_{0.1}MnO_x$	55.7		50	80	_	100	
α -MnO $_2$	80.6		$\sim \! 80$	\sim 110	126	\sim 155	127
β -MnO ₂	55.7		\sim 95	\sim 150	169	\sim 185	
Ag/α - MnO_2	64.2		\sim 45	~75	90	\sim 120	
Ag/β-MnO $_2$	40.0		~35	\sim 65	80	\sim 115	
α-MnO ₂	51.1	Soot	492	547	602	_	62
5Co-MnO ₂	50.2		436	513	567	_	
10Co-MnO ₂	51.7		420	475	546	_	
20Co-MnO ₂	50.7		479	528	586	_	
5Ni5Co-MnO ₂	58.3		379	445	513	_	
5Cu5Co-MnO ₂	59.4		368	431	485	_	
α-MnO ₂	52.7	Benzene	243	301	345	~375	31
α-MnO ₂ @Co ₃ O ₄	58.5		205	227	247	$\sim \! 265$	
α -MnO ₂	52.7		243	301	\sim 350	380	121
α-MnO ₂ @NiO	88.9		233	273	~ 300	320	
α-MnO ₂	_	Toluene	\sim 186	\sim 210	\sim 220	\sim 230	109
4% Ag/α-MnO ₂	_		_	\sim 195	\sim 215	\sim 220	
α-MnO ₂	39.9		214	\sim 230	237	\sim 245	83
α-MnO ₂ -110	_		_	142	170	200	87
α-MnO ₂ -210	_		_	88	109	140	
α -MnO ₂ -310	_		_	130	170	200	
α-MnO ₂	60.6		$\sim \! 240$	264	276	\sim 285	120
α-MnO ₂ @Co ₃ O ₄	54.9		$\sim \! 205$	220	229	\sim 235	
α-MnO ₂	93.1	Dimethyl ether	200	\sim 230	274	\sim 290	27
α -MnO ₂ (1 \sim 3 μ m)	_	·	176	_	_	250	105
α -MnO ₂ (4 \sim 8 μ m)	_		167	_	_	240	
α -MnO ₂ (6–10 μ m)	_		170	_	_	250	
α-MnO ₂ -100	87.9	Formaldehyde	\sim 80	125	\sim 145	150	86
α -MnO ₂ -110	119.5	·	\sim 50	100	\sim 125	130	
α -MnO ₂ -310	135.3		_	35	\sim 55	65	

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In addition, various studies have been conducted to improve the catalytic activity of MnO₂-based nanowires for CO oxidation. In order to achieve this goal, effective strategies including element doping, surface engineering and combination with other active substances have been extensively conducted. Gao et al.61 found that the hydrothermal doping of Cu would significantly increase CO oxidation activity (TOF = 9.1×10^{-3} $\rm s^{-1}$ at 70 °C) and water resistance of α -MnO₂ nanowires. As for γ-MnO₂, Zn-doped MnO₂ could achieve the 90% CO conversion at 160 °C and perform the best CO oxidation activity among Cu, Zn, Mg, Co, Ni, Ca, Al, Fe, and La-doped γ-MnO₂. ¹²⁸ Besides, the surface engineering is considered as another effective method to improve the catalytic activity of MnO2. Li et al. 92 synthesized α-MnO₂ with a large number of surface open cells through acid treatment. The open cells were rich in adsorption sites for O_2 , thus enhancing the catalytic activity of MnO₂ for CO oxidation. Moreover, combining Au,⁵⁶ Ag,¹²⁷ CuO,^{69,84} etc. with MnO₂ nanomaterials can effectively improve CO oxidation efficiency. Xu et al. 127 investigated the CO oxidation activity over the α-MnO₂ nanowires supported Ag based catalysts and the T₉₀ of Ag/ α-MnO₂ below 100 °C could be achieved. Although many studies have been carried out to enhance the catalytic activity of MnO₂ for CO oxidation and the complete CO conversion could be achieved at -34 °C,56 the current research hotspot is still focused on the loading or doping noble/transition metals. The further explorations should be concentrated on the surface engineering or the rare earth metals modification.

4.2 Catalytic removal of VOCs

The volatile organic compounds (VOCs) typically refer to organic compounds with boiling points between 50 °C and 260 °C at atmospheric pressure (101.325 kPa) according to the World Health Organization. 129 Besides, most VOCs emitted into the atmosphere can cause the formation of secondary pollutants, such as tropospheric ozone, peroxyacetyl nitrate, and secondary organic aerosols. 130-132 Various means have been used to remove the VOCs, such as the physical adsorption, 133 catalytic oxidation, 134,135 photocatalytic degradation, 136,137 plasma catalytic oxidation, 138 and biological decomposition. 139 Among these strategies, the catalytic oxidation has been considered as one of the most effective ways owing to various advantages, such as high efficiency, less secondary pollutants, and low reaction temperature. As for the catalysts of VOCs oxidation, compared with precious metal catalysts, the transition metal oxides catalysts are considered to be more promising candidates owing to their low costs and excellent catalytic performances. 140 MnO2 based nanomaterials are widely investigated as the effective catalysts and/or supports in the fields of pollutant removal, energy storage, and water treatment due to the excellent oxygen storage/release capacities, adsorption performances, and redox performances.141

4.2.1 Benzene. Benzene is extensively used in the fields of basic chemical and petrochemical industries. However, it is also harmful to human health at high risk. It is classified as the human carcinogen causing leukemia by the WHO.129 Up to now, the supported noble metal based catalysts, such as Pt, Pd, Au, Ag based catalysts, 142-145 are well known as the active catalysts for the oxidation of the benzene at low temperature. However, the development of the low-cost catalysts for the oxidation of benzene is in greatly urgent demand and the MnO2 based catalysts are promising candidates due to facile availability.

Hu et al.146 found that the order of catalytic activities on benzene combustion over MnO2 with different phase structures was γ -MnO₂ > β -MnO₂ > α -MnO₂ > δ -MnO₂. The surface adsorbed oxygen species concentration and low temperature O2 desorption of these manganese oxides were in good agreement with the sequence of their catalytic performance on benzene combustion. Besides, the strategies such as metal doping and loading have been investigated to improve the catalytic activities on benzene combustion over MnO2. Liu et al.147 found that the Ce³⁺ and Cu²⁺ doped of MnO₂ nanosheet could significantly improve the activity of MnO₂ for benzene decomposition. For the pristine MnO2, benzene was hardly decomposed below 200 °C and only \sim 40% conversion was achieved at 400 °C. Whereas, as for the Ce-MnO2 and Cu-MnO2 catalysts, the benzene started to decompose around 100 °C and nearly all benzene could be removed around 250 °C. Moreover, the Cu-MnO2 catalyst also exhibited high resistance to hightemperature deactivation and water resistance during continuous long-term testing. Recently, Ma et al.148 synthesized the tungsten-doped MnO2 (W-MnO2) with excellent performance of the photo-assisted thermal catalytic oxidation/removal of benzene. They found that doping W could not only generate abundant oxygen vacancies in MnO2, but also produce strong covalent interactions with adjacent O atoms through W-O bridge bonds, thereby promoting O₂ polarization and electron transference.

As for the metal loading, Ye et al. 149 prepared nanosized α-MnO₂-supported silver catalysts for benzene oxidation. They found that the 5Ag/MnO2 catalyst performed the best activity of the benzene oxidation. Tang et al.31 modified one-dimensional MnO₂-based catalysts (wire-like, rod-like α-MnO₂ and β-MnO₂ microrods) by the Co₃O₄ nanoparticles (see Fig. 13) and investigated them as the catalysts for benzene oxidation. They found that the modified MnO2@Co3O4 composite exhibited better catalytic performance than the pristine MnO2. The specific conversion efficiencies of the modified material to benzene abided by the order of α -MnO₂ nanowires > α -MnO₂ nanorods > β-MnO₂ nanorods. The reason for this could be attributed to the enhanced low-temperature reducibility and abundant active surface adsorption of oxygen derived from the heterogeneous hybrid interface.

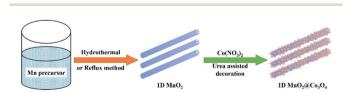


Fig. 13 Schematic process for the preparation of 1D MnO₂@Co₃O₄ hetero-nanostructures. Reproduced by Tang et al.31 with permission from Elsevier.

4.2.2 Toluene. Toluene could directly threaten the human health and safety because of its carcinogenicity and teratogenicity. 150,151 Therefore, the effective removal method of toluene should be explored in great urgency considering the harmful effects of toluene on the human health and the strict environmental regulations. Cheng et al. 83 found that α-MnO₂ nanowires performed much higher catalytic activity than the commercial MnO₂ counterpart toward toluene combustion. The reason for this could be attributed to the enhanced surface oxygen mobility and surface area of α-MnO2 nanowires, which were significantly better than the commercial MnO2. The possible oxidation reaction mechanism of toluene over α-MnO₂ catalyst was summarized in Fig. 14. Firstly, toluene adsorbed on α-MnO₂ catalyst surface. The adsorbed toluene would be subsequently oxidized into benzyl alcohol by surface lattice oxygen. Meanwhile, the resultant oxygen vacancies could be supplemented by gas-phase O₂, and active oxygen species (O₂/O₂⁻/O₂²⁻/O⁻/O²⁻) would be formed.86 The benzyl alcohol would be oxidized by active oxygen species into the benzaldehyde, and then further oxidized into the benzoic acid. Finally, the benzene ring would be destroyed by active oxygen species. After ring-opening, the

It has been reported that the catalytic performances of the toluene oxidation over the MnO_2 nanomaterials were strongly related to the crystalline phase structures. 91,124,152 Li *et al.* 91 prepared MnO_2 with different crystalline phases (β -, α -, γ -, and δ -). The results showed that catalytic toluene oxidation activities followed the sequence of $\delta > \gamma > \alpha > \beta$ -MnO₂. The morphology of the MnO₂ nanostructure also greatly influences the catalytic performance of the toluene oxidation. The previous study showed that the MnO₂ nanowire showed the most excellent toluene combustion catalytic activity ($T_{100} = 220$ °C) after loading silver among the MnO₂-based one-dimensional nanostructures (nanowire, nanorod, and nanotube). 30

unsaturated long chain enol and alkyne could be ultimately

transformed into the CO2 and H2O quickly.87

Besides, the metal loading and doping can also greatly enhance the catalytic performance in toluene oxidation removal. ¹⁵³, ¹⁵⁴ Dong *et al.* ¹⁵³ found that the introducing Na⁺ and

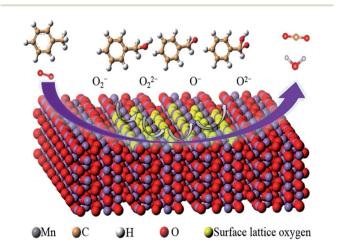


Fig. 14 Proposed mechanism of toluene degradation pathway on α -MnO₂. Reproduced by Huang *et al.*⁸⁷ with permission from Elsevier.

Ca²⁺ into MnO₂ promised the higher catalytic activity for toluene oxidation than pristine MnO₂. Specifically, the Ca-MnO₂ catalyst exhibited the best catalytic activity ($T_{90} = 215~^{\circ}\text{C}$) and possessed good water resistance. The outstanding catalytic performance of Ca-MnO₂ was closely related to the abundant acidic sites, high oxygen vacancy concentration, and the weak CO₂ adsorption capacity. Min *et al.*¹⁵⁴ found that transition metal (Ni and Co) doped α-MnO₂ and β-MnO₂ exhibited better catalytic performances in toluene oxidation removal owing to their lower crystallinities, more defects, larger specific surface areas, more oxygen vacancies, and better low-temperature redox ability than the pristine α-MnO₂ and β-MnO₂.

The catalytic performance of the toluene oxidation was also influenced by the interface between different metal oxides. Ren et al. 120 fabricated ZIF-derived Co₃O₄ grown in situ on 1D α-MnO₂ materials (as displayed in Fig. 15) and used it as the catalyst for toluene oxidation. They found that the α-MnO₂@Co₃O₄ could reduce the T₉₀ of toluene conversion to 229 °C, which was 47 °C and 28 °C lower than those of the pure α-MnO₂ nanowire and Co_3O_4 -b, respectively. The main reason for the enhanced catalytic activity could be attributed to the synergistic effect produced by the coupling interface constructed between α-MnO₂ and Co₃O₄. The specific reaction route of toluene oxidation on α-MnO₂@-Co₃O₄ catalyst could be illustrated as follows: toluene → benzoate species → alkanes containing oxygen functional group → CO₂ and H₂O. In addition, the α-MnO₂@Co₃O₄ catalyst also exhibited excellent stability and water resistance during the toluene oxidation.120 Zhang et al.155 found that the fluorine (F)doped titanium dioxide (TiO2) coupled with a small number of α-MnO₂ nanowires could effectively improve the photocatalytic degradation effect of toluene. Specifically, the toluene degradation efficiency before coupling was about 90%, and the toluene degradation efficiency after coupling was increased to 96%.

4.2.3 Phenol. Phenol is deemed as one of the most indispensable organic compounds widely used in various fields. However, it is also an aromatic environment pollutant and widely exits in the industrial wastewater, such as petroleum refinery, wood preservation, and coking. ¹⁵⁶ Phenol is a highly toxic substance, which has been listed as one of the most important organic pollutants with carcinogenic, mutagenic, and teratogenic hazards. ¹⁵⁷ Although MnO₂-based nanowires have been widely used in environmental catalysis, yet there are few studies investigating the application of MnO₂-based nanowire materials in water treatment. Dong *et al.* ¹⁵⁸ found out that

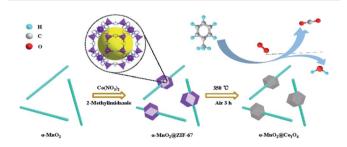


Fig. 15 Illustration of the fabrication of α -MnO₂@Co₃O₄ samples. Reproduced by Ren *et al.*¹²⁰ with permission from Elsevier.

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the β-MnO₂ nanowires possessed outstanding catalytic performance for phenol degradation. Saputra et al. 159 found that the α -MnO2 materials exhibited different activities in activating peroxymonosulfate to produce sulfate radicals for phenol degradation because of the variety in the phase structure and morphology. The results demonstrated that α-MnO₂ nanowire presented the highest activity with stable performance among the investigated nanomaterials. Then, they investigated the effect of phase structure of MnO2-based nanomaterials on the activities in activating oxone to generate sulfate radicals for phenol degradation. As can be seen in Fig. 16, the wire-like α -MnO₂ still exhibited higher activity than the rod-like β-MnO₂ and fiber-like γ-MnO₂ because of the large specific surface area and unique tunnel structure. Besides, the β-MnO₂ exhibited the lowest activity due to single tunnel and stable oxygen reducibility. Meanwhile, Peng et al. 160 also illustrated that α-MnO₂ nanowires performed higher activity than α-MnO₂ nanotubes in the catalytic phenol degradation. The probable reason for this was that α-MnO₂ nanowire possessed much greater surface area and lower negative surface charge density than the α-MnO₂ nanotube, further accounting for the higher catalytic activities. Liang et al. 161 synthesized the mesoporous Co₃O₄/α-MnO₂ catalyst exhibiting greatly high activity in peroxymonosulfate activation for phenol degradation with 100% conversion in 20 min. The stability tests also showed that the mesoporous Co₃O₄/MnO₂ catalyst presented excellent stability of phenol degradation in several runs without evident deactivation.

4.2.4 Formaldehyde. Formaldehyde (HCHO) has been extensively considered as one of the most harmful indoor VOCs closely related to the human health. As well known, most of the indoor decoration materials will release formaldehyde. Besides, the incomplete combustion of fuel and tobacco will also generate formaldehyde. The formaldehyde is not only a carcinogen but also greatly harmful to the eyes, nose, respiratory system, nervous system, and cardiovascular system. 162-164 Therefore, it is greatly urgent and necessary to effectively reduce the indoor HCHO to improve air quality and reduce public health risks. The catalytic oxidation of HCHO has been considered as a facile, green, and sustainable route. The noble metal catalysts commonly used for HCHO oxidation mainly

contain platinum. 165-167 Therefore, their widely industrial and commercial applications are severely restricted because of the high cost. Sekine et al.168 found that MnO2 could react with HCHO and release CO2 even at room temperature. This indicated that MnO₂ possessed great potential applications as the efficient catalysts in the catalytic oxidation of HCHO and could also be used as catalyst supports. Wang et al. 169 proposed a possible HCHO oxidation mechanism over the partially crystallized mesoporous MnOx catalyst under dry condition based on the MvK mechanism. As shown in the Fig. 17, firstly, the free oxygen molecules can be captured by oxygen vacancies on the surface of the catalyst. Then, the captured oxygen molecules are stripped and further decomposed into active oxygen species (i.e., adsorbed oxygen: Oads); Secondly, Mn3+ is oxidized into Mn⁴⁺ by O_{ads} and meanwhile one electron is released to O_{ads} to produce O⁻.170,171</sup> Thirdly, the adsorbed HCHO on the surface of manganese oxide is oxidized into the HCOOH intermediate by the O⁻. During this process, an electron will transfer from O⁻ to manganese cations and reduce Mn⁴⁺ to Mn³⁺ at the same time. Subsequently, the HCOOH intermediate further decomposes into H⁺ and HCOO⁻. The HCOO⁻ subsequently reacts with another Oads to produce HCO3- and HCO3- is finally degraded into H₂O and CO₂.

Li et al.174 reported that the sphere-like mesoporous MnO2 exhibited good catalytic activity and reusability for the formaldehyde gas oxidation and the formaldehyde purification efficiency could reach 99% after reacting at room temperature for 2 hours. Zhang et al.94 studied the catalytic activity of formaldehyde oxidation over the MnO2 nanomaterials with different phase structures (α-, β-, γ - and δ-). It was found that the δ-MnO₂ catalyst performed the best activity among these catalysts and could achieve the complete conversion of the HCHO at 80 °C, which was much lower than the α , β , and γ -MnO₂ at 125 °C, 200 °C, 150 °C, respectively. Besides, previous researches revealed that the Au-doped¹⁷⁵ and Ag-loading¹⁷⁶ α-MnO₂ nanorods exhibited superior catalytic performances of HCHO oxidation. The 100% conversion of HCHO could be achieved at 75 °C and 80 °C over the Au-doped and Ag-loading α-MnO₂ nanorods, respectively. Rong et al.86 prepared (310) facet

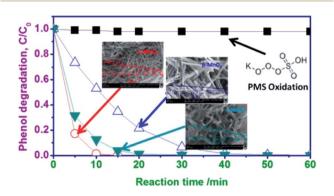


Fig. 16 Phenol degradation of MnO2-based nanomaterials with different phase structures. Reproduced by Saputra et al.29 with permission from ACS

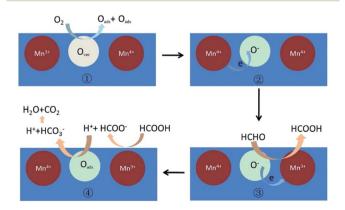


Fig. 17 The possible mechanism of catalytic oxidation of HCHO to CO_2 on partially crystallized mesoporous MnO_x under dry condition. Reproduced by Guan et al. 173 with permission from Elsevier.

exposed \$\alpha\$-MnO\$_2 nanowire catalyst through crystal facet engineering with superior HCHO oxidation activity. It could completely convert HCHO into CO\$_2\$ at 60 °C and achieve 86% conversion rate of 0.53 mg m^-3 HCHO at room temperature. He et al.\$^{177}\$ enhanced the catalytic oxidation of HCHO at ambient temperature over the \$\alpha\$-MnO\$_2\$ with four well-defined morphologies (nanowire, nanotube, nanorod, and nanoflower) with the help of the mechanical vibration. Among them, \$\alpha\$-MnO\$_2\$ nanowires exhibited the best catalytic activity with 100% conversion of 125 ppm HCHO at ambient temperature owing to the high oxygen vacancy concentration.

4.2.5 Methyl mercaptan. Methyl mercaptan (CH₃SH) is a highly toxic and corrosive sulfur-containing VOC (S-VOCs). It is widely released from sewage treatment and sanitary landfill. The exposure of CH₃SH at few ppm-level can make the human feel unpleasant and dozens of ppm-level can cause significant poisoning. 179,180 In these years, the catalytic removal of CH₃SH has been extensively studied. Catalytic combustion technology is considered as one of the most efficient technologies to convert S-VOCs into less toxic products (CO₂, SO₄²⁻, etc). But the temperature of catalytic combustion technology is usually higher than 300 °C, which consumes high energy and leads to the sintering of catalysts. 181-185 Currently, catalytic ozonation has been recognized as a promising approach owing to its advantages of high efficiency and complete oxidation of S-VOCs under mild conditions. 186,187 In most studies, supported noble metals (Au, Ag, Pt and Pd, etc.) and low-cost metal oxides like NiO, Fe₂O₃/Fe₃O₄, MnO₂, and Co₃O₄ have been developed as efficient catalysts for the catalytic ozonation of S-VOCs.187 MnO₂ is the most widely studied due to its plentiful valence states, versatile structures, high stability, and low cost.

The oxygen vacancies in MnO2 are usually considered as the active sites for O₃ adsorption and catalysing ozonation. 188 Fig. 18 shows the adsorption of CH₃SH over the MnO₂ catalyst and the mechanism of catalytic ozone. 93 O3 can be captured and decomposed by the structural defects on the MnO2 surface, then transformed into activate oxygen species (O2-/O22-), and quickly evolved into 'O₂⁻/'OH/¹O₂ through a chain cycle reaction, which can directly participate in CH₃SH and adsorbed CH₃S⁻ oxidation. It is desirable to obtain highly active crystal facets with abundant oxygen vacancies through surface engineering to improve the catalytic activity. He et al. 93 prepared α -MnO2 nanowire with different crystal facets exposed and successfully employed them to catalyse the ozonation of CH₃SH. The synthesized 310-MnO₂ catalyst performed higher activity than the 110-MnO2 and 100-MnO2. In addition, previous researches found that loading the metal active sites on MnO2 nanomaterials could also enhance the ozonation catalysis of CH₃SH.^{187,189} Xia et al.¹⁸⁷ prepared Ag deposited threedimensional MnO2 porous hollow microspheres (Ag/MnO2 PHMSs). The optimal 0.3% Ag/MnO₂ PHMSs could completely degrade 70 ppm CH₃SH within 600 seconds, displaying much higher efficiency than that of the pristine MnO₂ PHMSs support (79%). Additionally, the catalyst retained long-term stability and could be facilely regenerated to its initial activity with ethanol and HCl. Yang et al. 189 synthesized urchin-like oxygen vacancyrich (Vo) hollow-structured MnO2 with the loading of CuO

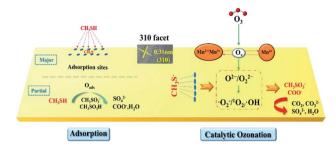


Fig. 18 Mechanism of adsorption and catalytic ozonation toward CH_3SH by $310-\alpha$ -MnO₂ catalysts. Reproduced by He *et al.*⁹³ with permission from ACS.

nanoparticles on the surface (CuO/V_O-MnO₂). The well-dispersed CuO on the surface of urchin-like hollow MnO₂ enhanced the chemisorption of CH₃SH, thus promoting the efficient decomposition of CH₃SH on the CuO/V_O-MnO₂. Among the as-prepared CuO/V_O-MnO₂ catalyst, the 5CuO/V_O-MnO₂ realized the optimum CH₃SH removal efficiency (98.5%) within 1200 s reaction under 25 °C, which was obviously higher than that of individual MnO₂ (70.7%) and CuO (57.0%).

However, there are few researches about the wire-like MnO₂ for the ozonation of CH₃SH except for the study of He.⁹³ In view of the strong interaction between wire-like MnO₂ and noble/ transition metals, more attentions will be attributed to the metal loading/doping of MnO₂ nanowire for the ozonation of CH₃SH in the future research.

4.3 Ozone

Ozone (O₃) is a light blue gas with special odor and strong oxidizing ability. O₃ usually can accomplish the complete oxidation of VOCs at room temperature. Therefore, the ozone is widely used as the oxidant in environmental treatment. However, when the amount of the pollutants, such as VOCs, are very large, the balance of ozone in the atmosphere will be broken, leading to the ozone pollution. Besides, the exposure to low-level ozone usually can cause serious effects on the human body's heart, lungs, respiratory tract, and cardiovascular system. ^{190–193} The catalysts used for the degradation of ozone can be divided into noble metals, ^{194,195} transition metal oxides ^{196–201} and noble transition compounds. ²⁰² In the view of the cost and large-scale application, the studies on the catalytic decomposition of ozone have been mainly focused on transition metal oxides, especially MnO₂.

 α -MnO $_2$ is a newly emerging material for catalytic decomposition of ozone. Jia *et al.*¹⁴¹ investigated the ozone removal activity over the MnO $_2$ with different phase structures (α , β , and γ). They found that α -MnO $_2$ performed the highest ozone removal efficiency. Zhu *et al.*²⁰³ developed a hierarchical structure consisted of graphene encapsulating α -MnO $_2$ nanofiber to address the challenges of the low stability and water inactivation during ozone decomposition. The optimized catalyst exhibited high ozone conversion efficiency of 80% and excellent stability over 100 h under a relative humidity (RH) of 20%. Even though the RH was as high as 50%, the ozone conversion also

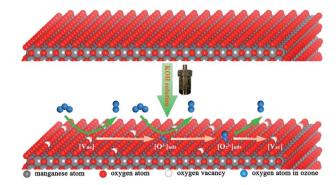


Fig. 19 Schematic of ozone catalytic decomposition on the K-rich MnO₂. Reproduced by Zhu *et al.*⁸² with permission from ACS.

could reach 70%, well beyond the performance of α-MnO₂ nanofiber. Zhang et al.155 found that introducing α-MnO2 nanowires into the fluorine (F)-doped titanium dioxide (TiO₂) could not only improve the photocatalytic degradation of toluene but also remove almost the total O₃ in the system. As the comparison, only 15.8% of O₃ could be removed by the pristine F-TiO₂ catalyst without mixing with α-MnO₂. This indicated that α-MnO₂ nanowire was an excellent catalyst for O₃ decomposition. Previous study showed that the oxygen vacancies on MnO₂ nanomaterials were active sites for ozone adsorption and further decomposition,199 which largely determined the catalytic degradation activity of MnO₂. Zhu et al. 82 developed the α-MnO₂ nanowire with high K⁺ content in tunnel structure through the simple KOH solution post-treatment. As shown in Fig. 19, the substantial increase in K⁺ content reduced the formation energy of oxygen vacancies, which was further conducive to the formation of oxygen vacancies in the crystal lattice. As a result, the ozone removal performance was improved by doping K^+ . However, peroxide species (O_2^{2-}) could accumulate on the surface of the catalyst and further evolve into relatively stable oxygen, resulting in the decrease in the ozone removal rate. Therefore, the accumulation of intermediate oxygen was a key factor limiting the high efficiency and sustainability of ozone decomposition. Liu et al.204 prepared cerium-modified todorokite-type manganese dioxides (Ce-MnO₂). The as-obtained catalyst showed greatly improved stability, which could keep ~98% of removal efficiency for \sim 115 ppm of O₃ within 5 h under a very high space velocity of 1200 L g⁻¹ h⁻¹ at room temperature. Besides, the Ce-MnO₂ catalyst also exhibited highly stable O3 removal efficiency at temperature as low as 0 °C.

5. Summary and prospect

MnO₂-based nanowires are becoming one of the most popular and promising catalysts in environmental applications due to their high catalytic performance, low cost and environmental friendliness. This review systematically summarizes the preparation methods of MnO₂-based nanowires, and the effects of phase structure, crystal facet, and morphology on their environmentally catalytic performance. In addition, this review also

summarizes their applications in environmental pollution control, such as CO oxidation, removal of VOCs, and the decomposition of O_3 .

- (1) Hydrothermal is a flexible and diverse preparation method, which can facilely control the phase structure, morphology, and exposed crystal facets of the product by changing hydrothermal reaction conditions and has been widely used in laboratory research of MnO₂ nanowires. As for the reflux method, it has various advantages (e.g. simple operation procedure, mild reaction condition, and low cost) and is suitable for the large-scale industrial synthesis. However, it is difficult for the sol–gel method alone to obtain wire-like MnO₂-based nanomaterials. Therefore, it is often used in combination with template method to prepare highly ordered MnO₂ nanowires. However, the employment of the templates will increase the cost of the preparation.
- (2) Crystal facet engineering is the research hotspot in the field of MnO₂ nanowires. Compared with the influences of phase structure and morphology, it has more significant impact on the catalytic activity of MnO₂ nanowires in environmental catalysis.
- (3) Doping and/or loading the metals or their oxides can effectively improve the chemical bond strength, phase structure, and electronic structure of the MnO₂ nanowires. As a result, the catalytic performance will be improved by increasing the fluidity of oxygen.

Up to now, lots of MnO₂-based nanowire material modulation strategies have been developed and their performances in the fields of environmental catalysis have also been promoted. However, the environmental applications of MnO₂-based nanowire materials are still at the early stage with various challenges and have a long way to go before the practical applications, specifically in the following aspects.

- (1) The complex crystal structures and the morphology diversity of MnO_2 result in challenging obstacles in obtaining pure phase structures and uniform morphologies of MnO_2 nanowires. Therefore, it is urgent to develop stable and efficient strategies to fabricate MnO_2 nanowires in single-crystalline solids with uniform morphology. Considering the remarkable improvement of the catalytic oxidation ability of MnO_2 nanowire by the crystal facet engineering, novel synthesis strategies for MnO_2 nanowire exposed a high proportion of specific crystal facet should be investigated in depth.
- (2) The crystal facet engineering of MnO₂ nanowire is mostly focused on the catalysis of VOCs. It can be predicted that it will also have great potential application in catalytic CO oxidation and ozone degradation. However, there are few studies in these areas. Different crystal facets have different catalytic oxidation performances toward specific VOCs. Therefore, it is of great urgency and necessity to systematically investigate the special functions of each crystal facet of MnO₂, and finally verify the types of VOCs matched.
- (3) Previous studies mainly focused on the noble metals (Au and Ag) and transition metals (Fe, Co, Ni, and Cu) loading or doping. However, few studies have focused on the modification of MnO₂ nanowire by loading or doping rare earth metals (La, Ce, Pr, and Sm). In view of the improvement of the O₃ removal

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efficiency of MnO₂ at low temperature by the cerium doping, the effect of catalytic degradation of other air pollutants by the rare earth metals modification should be explored in the future.

(4) Although MnO₂-based nanowire materials as the supports or the efficient catalysts are gradually emerging in the field of environmental catalysis, yet there is still giant gap between the laboratory results and actually industrial requirement in the aspects of the catalytic performance, long-term stability, and water resistance of removing CO and VOCs at relatively low temperature compared with traditional noble metal catalysts.

Author contributions

LX: conceived ideas, made comments, edited; YX: investigation, writing - original draft; GC, CW, NW: assisted YX in literature research and summary; LX, MC, XH: investigation, supervision, funding acquisition. All authors discussed the results and contributed to the final manuscript.

Conflicts of interest

There are no conflicts to declare.

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