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# Recent progresses in the synthesis of MnO<sub>2</sub> nanowire and its application in environmental catalysis

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Nanostructured MnO<sub>2</sub> with various morphologies exhibits excellent performance in environmental catalysis owing to its large specific surface area, low density, and adjustable chemical properties. The one-dimensional MnO<sub>2</sub> nanowire has been proved to be the dominant morphology among various nanostructures, such as nanorods, nanofibers, nanoflowers, etc. The syntheses and applications of MnO<sub>2</sub>-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 MnO<sub>2</sub> 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 MnO<sub>2</sub> 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 MnO<sub>2</sub> 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 MnO<sub>2</sub> nanowires in the field of environmental catalysis, such as CO oxidation, the removal of VOCs, denitrification, etc., have been also summarized. The application of MnO<sub>2</sub> 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 MnO<sub>2</sub> 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.<sup>1,2</sup> 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.<sup>3-6</sup> Besides, it is also a weak direct greenhouse gas and has an

important indirect effect on global warming.<sup>7-10</sup> Generally, CO is mainly derived from the incomplete combustion of fuels.<sup>11,12</sup> As for the VOCs, they commonly include formaldehyde, benzene, toluene, xylene, etc.<sup>2</sup> 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<sub>2.5</sub> and O<sub>3</sub> 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,<sup>13,14</sup> Pt,<sup>15-17</sup> Pd,<sup>18</sup> and Rh<sup>19</sup>) supported on particular metal oxides (CeO<sub>2</sub>, Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>) with excellent oxygen storage capacities usually perform high

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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 ( $\text{Co}_3\text{O}_4$ ,<sup>20,21</sup>  $\text{CuO}$ ,<sup>22</sup>  $\text{MnO}_2$ ,<sup>23</sup> and  $\text{CeO}_2$  (ref. 24)) performed excellent catalytic activity for CO oxidation in the past decades. Among them,  $\text{MnO}_2$  has been extensively investigated due to various advantages, such as low price, environmental friendliness, and relatively high activity.<sup>25,26</sup> With the continuous studies on  $\text{MnO}_2$  based materials, it has been found that  $\text{MnO}_2$  based catalysts usually perform good oxidation activities for the VOCs, such as formaldehyde, toluene, benzene, dimethyl ether, *etc.* Besides, the catalytic oxidation ability of  $\text{MnO}_2$  can be greatly improved through crystal facet exposure engineering and regulating the loading methods.

Compared with the traditional bulk  $\text{MnO}_2$ , the nanostructured  $\text{MnO}_2$  materials usually perform better physicochemical characteristics, such as the higher specific area, lower density, and more adjustable chemical nature. Furthermore, various studies have shown that  $\text{MnO}_2$  with nanowire morphology usually perform high surface areas and strong metal-support interactions.<sup>27–31</sup> Therefore, the nanowire is the dominant morphology among the  $\text{MnO}_2$ -based nanostructured materials. Compared with  $\text{MnO}_2$  nanorods,  $\text{MnO}_2$  nanowires commonly possess 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 ether<sup>27</sup> and plasma catalytic oxidation of toluene.<sup>28</sup> Saputra *et al.*<sup>29</sup> found that  $\text{MnO}_2$  nanowire displayed much higher activity than the  $\text{MnO}_2$  nanorod and nanofiber counterparts in activating oxygen ketones to degrade phenol. In addition to this, compared with rod-shaped and tubular  $\text{MnO}_2$ , the  $\text{MnO}_2$  nanowire as the support behaved stronger interaction with Ag and displayed the much higher reactivity of toluene oxidation.<sup>30</sup> The  $\alpha$ - $\text{MnO}_2$  nanowire also displayed the best catalytic activity toward gaseous benzene oxidation among the  $\text{MnO}_2$ -based nanomaterials with different morphologies (*e.g.*, wire and rod-like  $\alpha$ - $\text{MnO}_2$ ,  $\beta$ - $\text{MnO}_2$  micro-rods) even after decorating  $\text{Co}_3\text{O}_4$  nanoparticles.<sup>31</sup>

In recent years, more and more advanced and important materials have been developed for the applications of  $\text{MnO}_2$ -based nanomaterials in the removal of environmental pollutants,<sup>32,33</sup> biosensing,<sup>34</sup> theranostic,<sup>35</sup> especially in the field of electrochemistry.<sup>36–38</sup> For example, Li *et al.*<sup>37,38</sup> synthesized  $\alpha$ - $\text{MnO}_2$  nanowires with outstanding circulation stability, demonstrated rate performance, and high specific capacitance for supercapacitor electrode. Therefore, the previous reviews of  $\text{MnO}_2$ -based nanomaterials were mainly focused on their applications in electrochemistry.<sup>39–43</sup> However, there were few reviews paid close attention to their environmental applications. Yang *et al.*<sup>44</sup> systematically summarized the environmental applications of  $\text{MnO}_2$ -based materials. But they did not specially highlight the unique advantages of  $\text{MnO}_2$ -based nanowire materials, which have been considered as the basic assembly unit of two-dimensional or three-dimensional

structure complex/heterostructure materials of  $\text{MnO}_2$  (ref. 45) and normally have higher catalytic activity compared with  $\text{MnO}_2$ -based nanomaterials in other morphologies.<sup>27–30</sup> Meanwhile, the previous discussions about  $\text{MnO}_2$ -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  $\text{MnO}_2$ -based nanowire materials in the field of environmental catalysis. A systematic overview of frontier scientific research on the modulation of  $\text{MnO}_2$ -based nanowire materials for environmental catalysis application is urgent for the rational design and fabrication of high-efficiency  $\text{MnO}_2$ -based nanowire materials. Therefore, this review comprehensively summarizes the synthesis methods of  $\text{MnO}_2$ -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  $\text{MnO}_2$ -based nanowire materials in the field of environmental catalysis are also covered in this review. With the in-depth research on  $\text{MnO}_2$ -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 $\text{MnO}_2$ -based nanowires

There are various preparation methods of  $\text{MnO}_2$  nanomaterials, such as the liquid phase precipitation method,<sup>46,47</sup> reflux method,<sup>48</sup> electrodeposition method,<sup>49</sup> hydrothermal method,<sup>50–53</sup> sol-gel method,<sup>54,55</sup> template method,<sup>56</sup> thermal decomposition method,<sup>57</sup> and so on. As a result, the phase structures and chemical characteristics of  $\text{MnO}_2$  nanomaterials fabricated by different methods will be completely different. Similarly, the synthesis of  $\text{MnO}_2$ -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  $\text{MnO}_2$ -based nanowires have been summarized in Table 1.

### 2.1 Hydrothermal synthesis method

The hydrothermal synthesis of  $\text{MnO}_2$ -based nanowires mainly involves oxidation–reduction reaction of  $\text{MnO}_4^-$  and/or  $\text{Mn}^{2+}$  or the phase transition of  $\text{MnO}_2$  precursor. The hydrothermal method usually involves several key parameters, including the reagent amount, reaction time, hydrothermal temperature, pH, and so on. Therefore, the  $\text{MnO}_2$ -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<sub>2</sub>-based nanowires

MnO <sub>2</sub> nanowire	Preparation method	Raw materials	Synthesis temperature (°C)	Synthesis time (h)	Length	Diameter (nm)	BET (m <sup>2</sup> g <sup>-1</sup> )	Reference
α-MnO <sub>2</sub>	Hydrothermal method	MnSO <sub>4</sub> ·H <sub>2</sub> O, KMnO <sub>4</sub>	150	12	2.5 μm	20–40	61.0	82
	Hydrothermal method	KMnO <sub>4</sub> , NH <sub>4</sub> Cl	200	48	Several μm	100–200	53.1	61
	Hydrothermal method	MnSO <sub>4</sub> ·H <sub>2</sub> O, (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	140	12	0.4–5 μm	5–20	148.0	29
	Hydrothermal method	δ-MnO <sub>2</sub> , H <sub>2</sub> SO <sub>4</sub>	100	24	250–500 nm	30–60	93.1	27
	Hydrothermal method	KMnO <sub>4</sub> , CH <sub>3</sub> COOH	140	12	6–10 μm	30–60	39.9	83
	Reflux method	δ-MnO <sub>2</sub> nanosheets	80–90	90–120	>10 μm	20–30	53.2	58
	Sol-gel template method	AAO template, Mn (CH <sub>3</sub> COO) <sub>2</sub> , citric acid	400	12	500–700 nm	70	—	54
β-MnO <sub>2</sub>	Hydrothermal method	MnSO <sub>4</sub> ·H <sub>2</sub> O, (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	140	12	1.5–2.5 μm	60–100	55.7	84
	Hydrothermal method	Mn (NO <sub>3</sub> ) <sub>2</sub> , O <sub>3</sub>	200	8	2–5 μm	6–12	73.5	58
γ-MnO <sub>2</sub>	Hydrothermal method	MnSO <sub>4</sub> ·H <sub>2</sub> O, (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	90	24	—	—	—	85
δ-MnO <sub>2</sub>	Hydrothermal method	MnSO <sub>4</sub> ·H <sub>2</sub> O, KMnO <sub>4</sub>	240	24	—	—	—	—
α-MnO <sub>2</sub> -100	Hydrothermal method	MnSO <sub>4</sub> ·H <sub>2</sub> O, (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , KNO <sub>3</sub>	120	20	Several μm	15–20	87.9	86
α-MnO <sub>2</sub> -110	Hydrothermal method	KMnO <sub>4</sub> , (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	180	24	—	45–50	119.5	—
	Hydrothermal method	KMnO <sub>4</sub> , (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	180	24	100–500 nm	10–50	—	87
α-MnO <sub>2</sub> -210	Hydrothermal method	MnCO <sub>3</sub> , HNO <sub>3</sub> , (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , H <sub>2</sub> SO <sub>4</sub>	140	2	100–500 nm	10–50	—	—
α-MnO <sub>2</sub> -310	Hydrothermal method	KMnO <sub>4</sub> , (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	180	24	100–500 nm	10–50	—	—
	Hydrothermal method	KMnO <sub>4</sub> , (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	180	24	Several μm	15–20	135.3	86

DeGuzman *et al.*<sup>50</sup> pointed out that pH and temperature could affect the final phase structure of MnO<sub>2</sub> in the synthesis of fibrous α-MnO<sub>2</sub> nanomaterials and α-MnO<sub>2</sub> would transit into β-MnO<sub>2</sub> when the temperature was kept above 120 °C. However, Wang *et al.*<sup>51</sup> found that the effects of pH and temperature were not significant. In their study, 1D MnO<sub>2</sub> 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 (KMnO<sub>4</sub> and MnSO<sub>4</sub>) 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-MnO<sub>2</sub> nanowire. For example, the optimal hydrothermal temperature was located between 120 °C and 160 °C when using KMnO<sub>4</sub> and MnSO<sub>4</sub>·H<sub>2</sub>O as raw materials;<sup>58–60</sup> whereas, the optimal hydrothermal temperature was 200 °C when using KMnO<sub>4</sub> and NH<sub>4</sub>Cl as the precursors.<sup>61–63</sup> 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 MnO<sub>2</sub> crystal forms have different sizes and need different amounts of cations to stabilize.<sup>64</sup> Zhang

*et al.*<sup>53</sup> showed that the phase structure of MnO<sub>2</sub> and the aspect ratio of the final product were greatly depended on the concentration of ions in the reaction system, especially K<sup>+</sup>. Because the high concentration of K<sup>+</sup> could be used as the effective template, which was more conducive to the synthesis of α-MnO<sub>2</sub> nanowire.<sup>53</sup> Wang *et al.*<sup>51</sup> believed that the layer structure of δ-MnO<sub>2</sub> tended to curl under the high temperature and pressure, which was considered as the determinant step for the formation of 1D nanostructures of MnO<sub>2</sub>. Zhang *et al.*<sup>53</sup> also indicated that prolongating hydrothermal time could drive the self-assembly of α-MnO<sub>2</sub> into bundles and then transform into β-MnO<sub>2</sub>. Therefore, the possible synthesis route of MnO<sub>2</sub>-based nanostructures was described in Fig. 1. First, the MnO<sub>x</sub> units appear in the solution and the δ-MnO<sub>2</sub> with the layer structure is then formed through a series of condensation reactions. δ-MnO<sub>2</sub> tends to curl under high temperature and high pressure. When K<sup>+</sup> concentration is high, α-MnO<sub>2</sub> can be formed; otherwise, β-MnO<sub>2</sub> can be formed. With the prolonging of hydrothermal time, the [2 × 2] tunnel structure of α-MnO<sub>2</sub> directly collapses into the [1 × 1] tunnel structure of β-MnO<sub>2</sub>.<sup>53</sup> Wei



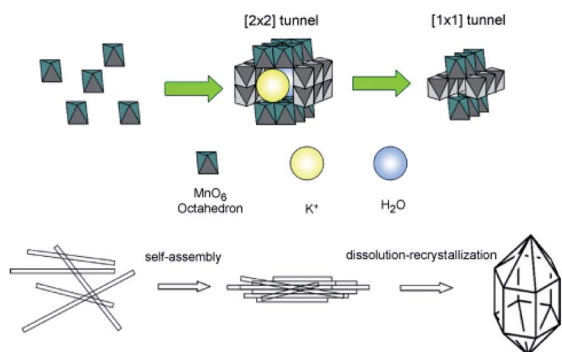


Fig. 1 Schematic illustration of the self-assembly of  $\alpha$ - $\text{MnO}_2$  nanowires into bundles and their subsequent phase transformation to  $\beta$ - $\text{MnO}_2$  microcrystals under prolonged hydrothermal conditions. Reproduced by Zhang *et al.*<sup>53</sup> with permission from Elsevier.

*et al.*<sup>52</sup> studied the hydrothermal synthesis of  $\text{MnO}_2$ -based nanowires through the phase transition of granular  $\text{MnO}_2$  precursor. They synthesized  $\alpha$ - $\text{MnO}_2$  and  $\beta$ - $\text{MnO}_2$  single crystal nanowires by the hydrothermal treatment of  $\gamma$ - $\text{MnO}_2$  at different temperatures. This method not employing catalysts or templates could be easily reproduced. Therefore, the hydrothermal synthesis of different crystal types of  $\text{MnO}_2$  nanowires with potential application prospects in large-scale could be realized.

Generally, the hydrothermal method of preparing  $\text{MnO}_2$ -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  $\text{MnO}_2$ -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.<sup>65</sup>

## 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  $\text{MnO}_2$  nanowires owing to various advantages, such as simple operation and mild reaction conditions. Kijima *et al.*<sup>66</sup> synthesized  $\text{MnO}_2$  with three different phase structures ( $\alpha$ -,  $\beta$ -, and  $\gamma$ -) by the acid digestion of  $\text{Mn}_2\text{O}_3$  under reflux conditions. The type of polymorph of  $\text{MnO}_2$  products was strongly dependent on the reaction temperature, type of acid used, and the concentration. When  $\text{H}_2\text{SO}_4$  was used as the acid, the  $\alpha$ - $\text{MnO}_2$  was inclined to form at higher  $\text{H}_2\text{SO}_4$  concentrations and lower reaction temperatures. In contrast, the  $\beta$ - $\text{MnO}_2$  was obtained at lower  $\text{H}_2\text{SO}_4$  concentrations and higher reaction temperatures. The  $\gamma$ - $\text{MnO}_2$  were formed at intermediate conditions. When  $\text{HNO}_3$  was used as the acid, only the  $\beta$ - $\text{MnO}_2$  and  $\gamma$ - $\text{MnO}_2$  could be formed. The  $\alpha$ - $\text{MnO}_2$  could not be obtained in the  $\text{HNO}_3$  solution. Compared with  $\gamma$ - $\text{MnO}_2$ , the  $\beta$ - $\text{MnO}_2$  formation

usually demanded higher reaction temperatures ( $>80^\circ\text{C}$ ) and higher concentrations of  $\text{HNO}_3$  ( $>10\text{ mol L}^{-1}$ ).<sup>66</sup> Chen *et al.*<sup>67</sup> synthesized transition metal doped  $\alpha$ - $\text{MnO}_2$  nanofibers by the reflux method. Compared to the pristine  $\text{MnO}_2$ , metal cation doped  $\text{MnO}_2$  materials had slightly higher surface areas and pore volumes, especially when the dopant content was relatively high. Jin *et al.*<sup>68</sup> synthesized  $\gamma$ - $\text{MnO}_2$  homogeneous nanofiber with the length of  $\sim 1\ \mu\text{m}$  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.*<sup>65</sup> prepared  $\delta$ - $\text{MnO}_2$  nanosheets by the reflux method and further deepened the morphological evolution and shape transformation into ultra-long  $\alpha$ - $\text{MnO}_2$  nanowires with extremely high purity by reflux. The length of the nanowire was observed to exceed  $10\ \mu\text{m}$ . 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  $\alpha$ - $\text{MnO}_2$  nanowires could be generated without using catalysts and stencils. The reflux method provides a promising preparation method of  $\alpha$ - $\text{MnO}_2$  nanowires in large scale.<sup>65</sup> May *et al.*<sup>69</sup> synthesized  $\alpha$ - $\text{MnO}_2$ -based nanowires and further studied the effect of doping methods on low-temperature CO oxidation of  $\text{CuO}/\alpha$ - $\text{MnO}_2$  catalysts based on the nitric acid reflux method of Uematsu *et al.*<sup>70</sup>

## 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  $\text{MnO}_2$  commonly includes various combinations of hydrated metal cations, such as manganese acetate ( $\text{MnAc}_2$ ) and citric acid,<sup>71</sup>  $\text{MnAc}_2$  and n-propyl alcohol,<sup>54</sup> tetrabutylammonium permanganate and methanol,<sup>72</sup> and  $\text{KMnO}_4$



Fig. 2 Preparation of gram level  $\alpha$ - $\text{MnO}_2$  nanowires from aqueous  $\text{KMnO}_4$ /ethyl acetate biphasic system and their different stages (a–f) in digital/FESEM images. Reproduced by Sinha *et al.*<sup>65</sup> with permission from ACS.





and fumaric acid ( $C_4H_4O_4$ ).<sup>73,74</sup> The structures of the obtained  $MnO_2$  are strongly depended on the molar ratio between the  $KMnO_4$  and the organic reducing agents.<sup>75</sup> For example, the 3 : 1 reactant ratio of  $KMnO_4$  to glucose favoured the cryptomelane ( $2 \times 2$  tunnel) synthesis, while the 5 : 1 ratio generated the layered birnessite-type material.<sup>72</sup> Hastuti *et al.*<sup>74</sup> synthesized irregular spherical  $\alpha$ - $MnO_2$  particles by the sol-gel method and discovered that transition metal ( $Fe^{3+}$ ,  $Cu^{2+}$ ) doping did not affect the phase structure but only changed the lattice parameters and morphology of the final product. Hashem *et al.*<sup>76</sup> prepared the  $\alpha$ - $MnO_2$  materials by redox reaction of  $KMnO_4$  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  $\sim 0.8$   $\mu m$ , and further aggregated to urchin-like balls. Hashemzadeh *et al.*<sup>71</sup> prepared  $\gamma$ - $MnO_2$  polymorph using the manganese acetate and citric acid as the raw reagents in the sol-gel way. The obtained  $\gamma$ - $MnO_2$  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  $MnO_2$  nanowire with different morphologies. Ghorbani *et al.*<sup>77</sup> successfully synthesized  $MnO_2$  nanowires with 45 nm in diameter using simple precursors, such as  $KMnO_4$  and  $NaNO_3$ , by sol-gel method. They found that the optimal annealing temperature for achieving crystalline structure and nanowire morphology was 600  $^\circ C$ . Chin *et al.*<sup>78</sup> successfully prepared  $MnO_2$  nanowires *via* the self-assembly of  $MnO_2$  nanoparticles using the sol-gel method with  $KMnO_4$  and  $Mn(ClO_4)_2$  as the precursors. The microstructure and morphology of sol-gel derived  $MnO_2$  nanowire were affected by the synthesis conditions and post synthesis heat treatment. Acidic pH value (pH 5.7) and calcination temperature at 300  $^\circ C$  were effective on achieving nanowire morphology and high surface area. Liu *et al.*<sup>79</sup> synthesized wire-like ion sieve  $MnO_2 \cdot 0.5H_2O$  with about 50–200 nm in diameter and 0.5–2  $\mu m$  in length using the sol-gel method. The ion sieve  $MnO_2 \cdot 0.5H_2O$  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 a better way to synthesize highly-ordered  $MnO_2$ -based

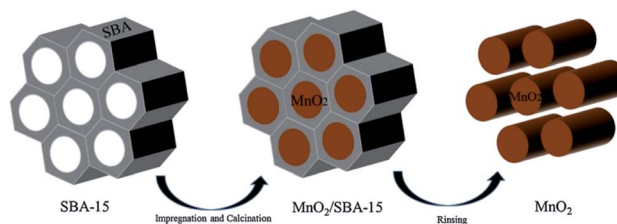


Fig. 4 Schematic representation of the preparation of  $MnO_2$  by SBA-15 template. Reproduced by Zhang *et al.*<sup>80</sup> with permission from Elsevier.

nanowires than the sol-gel itself.<sup>54,55</sup> As shown in Fig. 3, Tang *et al.*<sup>55</sup> used CTAB as the surfactant to obtain highly dispersed ultrafine  $MnO_2$  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.*<sup>54</sup> successfully prepared  $\alpha$ - $MnO_2$  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.*<sup>56</sup> used mesoporous silica SBA-15 as the hard template to prepare highly ordered array of mesoporous  $\beta$ - $MnO_2$  nanowires by the nano-casting method. Fig. 4 shows the schematic representation of the preparation of  $MnO_2$  by using the SBA-15 as the template.<sup>80</sup>

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.*<sup>81</sup> fabricated hierarchical  $MnO_2$  microfibers by using cotton as the template and  $KMnO_4$  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  $MnO_2$ -based nanowires and other metal oxide materials in the view of economical concern.

## 3. The factors affecting the catalytic performances of $MnO_2$ nanowires

### 3.1 Phase structure

The  $[MnO_6]$  octahedral unit is the basic building block for crystalline-phase  $MnO_2$  materials. As shown in Fig. 5, when  $[MnO_6]$  octahedral units are linked in different ways, the  $MnO_2$  can form a variety of polymorphs, such as  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ - $MnO_2$ .<sup>88–90</sup> Studies have found that the phase structure can

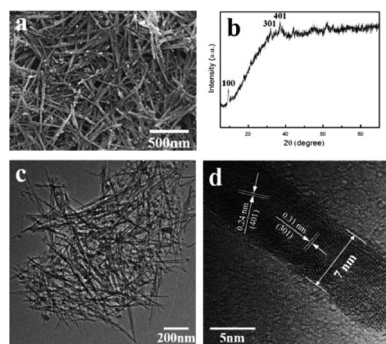


Fig. 3 (a) SEM image, (b) XRD pattern, (c) and (d) TEM images of  $MnO_2$  nanowire prepared by sol-gel approach. Reproduced by Tang *et al.*<sup>55</sup> with permission from Elsevier.



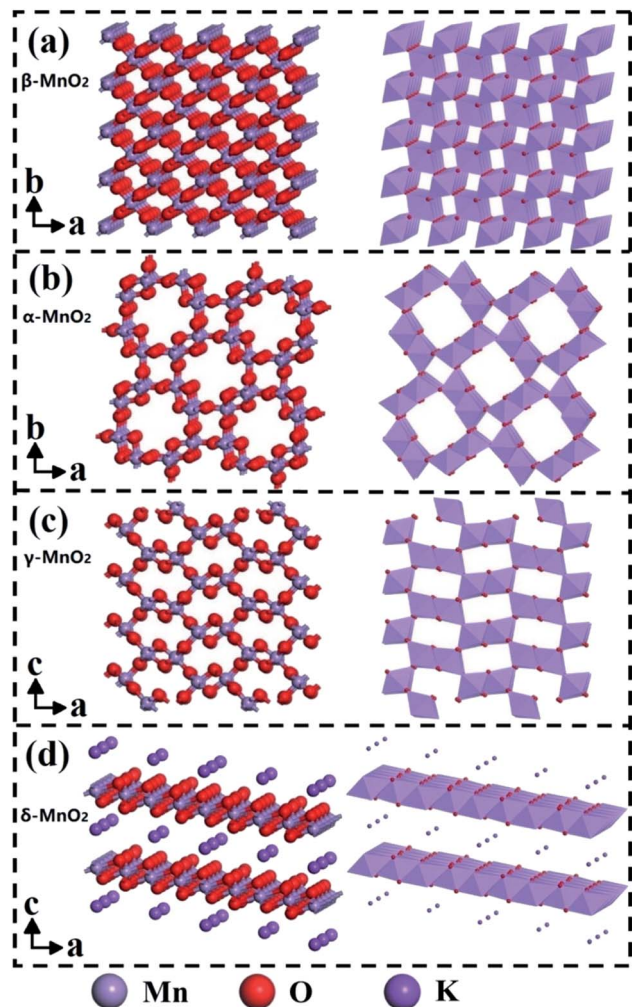


Fig. 5 Ball-stick and polyhedron representations of (a)  $\beta$ -, (b)  $\alpha$ -, (c)  $\gamma$ - and (d)  $\delta$ - $\text{MnO}_2$ . Reproduced by Li *et al.*<sup>91</sup> with permission from Elsevier.

significantly affect the catalytic activity of  $\text{MnO}_2$ , and both  $\alpha$ - $\text{MnO}_2$  and  $\delta$ - $\text{MnO}_2$  are the dominant phase structures of  $\text{MnO}_2$ -based catalytic nanomaterials.<sup>91–94</sup>

Specifically,  $\alpha$ - $\text{MnO}_2$  occupies more space than  $\beta$ -,  $\gamma$ -, and  $\delta$ - $\text{MnO}_2$  due to the double tunnel structure of  $[2 \times 2]$  and  $[1 \times 1]$ . 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  $\alpha$ - $\text{MnO}_2$  nanowires, thereby providing abundant oxygen adsorption sites for the reactants.<sup>92</sup> In addition,  $\alpha$ - $\text{MnO}_2$  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,  $\alpha$ - $\text{MnO}_2$  performs much better activity than other phase structures in catalytic reactions, such as CO oxidation,<sup>26</sup>  $\text{O}_3$  catalytic degradation,<sup>93</sup> plasma oxidation of toluene,<sup>28</sup> and degradation of phenol by activating oxyketone.<sup>29</sup>

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

toluene molecule to adsorb on the surface of  $\delta$ - $\text{MnO}_2$  and thereby behaves excellent activity in the catalytic oxidation of toluene.<sup>91</sup> As the comparison, the  $\alpha$ - $\text{MnO}_2$  performs weaker toluene oxidation activity due to the lower content of  $\text{Mn}^{4+}$  and lattice oxygen.<sup>91</sup> Besides,  $\delta$ - $\text{MnO}_2$  has also been proved to be the best crystalline phase structure for low-temperature catalytic oxidation of formaldehyde.<sup>94</sup>

$\beta$ - $\text{MnO}_2$  with  $[1 \times 1]$  tunnels have the most stable redox ability among these four phase structures. Besides, the surface area of  $\beta$ - $\text{MnO}_2$  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  $\gamma$ - $\text{MnO}_2$  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.<sup>95–97</sup> Recently, more and more studies have paid attention to the influence of specific crystal facets on their catalytic effects, such as  $\text{TiO}_2$ ,<sup>95</sup>  $\text{Fe}_2\text{O}_3$ ,<sup>96</sup>  $\text{CeO}_2$  (ref. 97) and  $\text{Co}_3\text{O}_4$ ,<sup>20</sup> 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  $\text{MnO}_2$ -based nanowires to the catalytic oxidation of VOCs, such as formaldehyde,<sup>86</sup> methylmercury<sup>93</sup> and toluene,<sup>87</sup> *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.<sup>98</sup> Many studies have been carried out on the  $\alpha$ - $\text{MnO}_2$  nanowires because  $\alpha$ - $\text{MnO}_2$  has highest activity among the four phase structures of  $\text{MnO}_2$ -based nanowires. The characteristic crystal facets of  $\alpha$ - $\text{MnO}_2$  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  $\text{O}_2$ ,  $\text{H}_2\text{O}$  (ref. 86) and  $\text{O}_3$ ,<sup>93</sup> *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.*<sup>86</sup> reported that the 310- $\alpha$ - $\text{MnO}_2$  could completely convert 100 ppm formaldehyde to  $\text{CO}_2$  at 60 °C, which was even better than some silver-based catalysts.<sup>99,100</sup> As shown in Fig. 7, the (310) facets with high surface energy could not only facilitate adsorption/activation of  $\text{O}_2$  and  $\text{H}_2\text{O}$  but also be beneficial to the generation of oxygen vacancies, which resulted in significant enhancement of HCHO oxidation activity. He *et al.*<sup>93</sup> reported that the 310- $\alpha$ - $\text{MnO}_2$  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





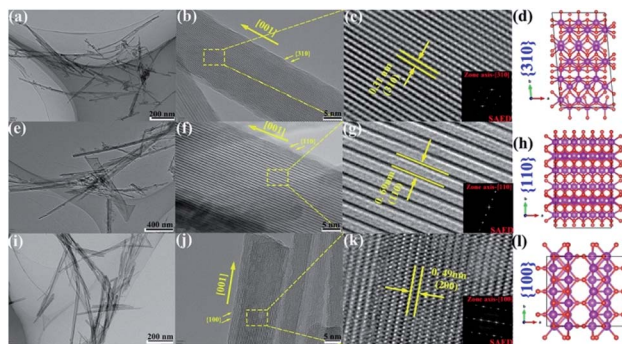


Fig. 6 TEM and HRTEM images of (a–c)  $\alpha$ -MnO<sub>2</sub>-310, (e–g)  $\alpha$ -MnO<sub>2</sub>-110, and (i–k)  $\alpha$ -MnO<sub>2</sub>-100. Atomic structure of the (d) {310}, (h) {110}, and (l) {100} surface of  $\alpha$ -MnO<sub>2</sub>. Small (red) spheres are oxygen and large (purple) are manganese. Reproduced by Rong *et al.*<sup>86</sup> with permission from ACS.

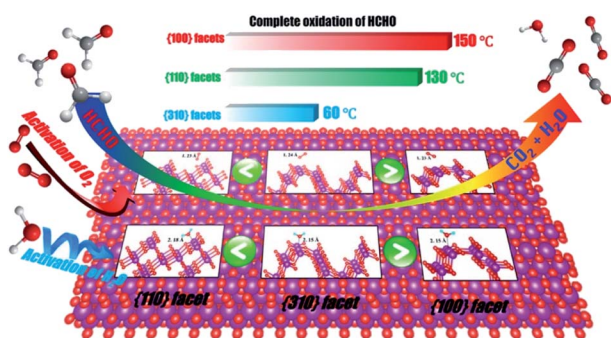


Fig. 7  $\alpha$ -MnO<sub>2</sub> nanowires with (100), (110) and (310) facets for HCHO oxidation. Reproduced by Rong *et al.*<sup>86</sup> with permission from ACS.

crystal.<sup>86</sup> Meanwhile, Huang *et al.*<sup>87</sup> found that (210) crystal plane with the lower surface activation energy (24.75 kJ mol<sup>-1</sup>) 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 MnO<sub>2</sub>-based nanowires is the key to improving the oxidation ability of MnO<sub>2</sub>-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 MnO<sub>2</sub>-based nanowires.

### 3.3 Morphology

As well known, the physiochemical properties of MnO<sub>2</sub> with different morphologies are often different.<sup>101,102</sup> The common one-dimensional structure of MnO<sub>2</sub> includes nanorods, nanotubes and nanowires. Among these morphologies, the MnO<sub>2</sub> nanowires occupies an important place. Because one-dimensional nanowires can be used as the basic assembly unit of two-dimensional or three-dimensional structure

materials.<sup>45</sup> Furthermore, the composite materials with novel structures and properties can be facily 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 W<sub>18</sub>O<sub>49</sub> nanowires is greatly affected by its aspect ratio;<sup>103</sup> the dielectric properties of BaTiO<sub>3</sub> nanowires also have close relationship with its length.<sup>104</sup> Therefore, the performance of the nanowire can be tuned by controlling the length or aspect ratio. Liao *et al.*<sup>105</sup> investigated the influence of the length of  $\alpha$ -MnO<sub>2</sub> nanowires on the catalytic combustion performance of dimethyl ether. The results revealed that the length of the nanowires would affect the redox property of  $\alpha$ -MnO<sub>2</sub> and the final catalytic combustion performance of dimethyl ether. Among them,  $\alpha$ -MnO<sub>2</sub> nanowires with medium length (4–8  $\mu$ m) 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.<sup>105</sup> Li *et al.*<sup>91</sup> prepared three kinds of  $\delta$ -MnO<sub>2</sub> with different crystallinities and morphologies. The complete toluene conversion was achieved at 250–275 °C for  $\delta$ -MnO<sub>2</sub> and the toluene conversion efficiency of  $\delta$ -MnO<sub>2</sub> 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 MnO<sub>2</sub> 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 MnO<sub>2</sub>-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.<sup>106</sup> 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.<sup>107</sup> 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 MnO<sub>2</sub>-based nanowire can be further improved by dispersing more active ingredients on its surface.

The studies related to the metal modification of MnO<sub>2</sub> usually starts with the loading of noble metals, such as Au and Ag. For example, Gu *et al.*<sup>56</sup> loaded Au nanoparticles on  $\alpha$ -,  $\beta$ -MnO<sub>2</sub> nanowires and developed Au/MnO<sub>2</sub> catalyst with extremely high activity and stability for CO oxidation at low temperature. The Au/ $\alpha$ -MnO<sub>2</sub> 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 °C, and slowly reached 100% at around –34 °C. The low-temperature (–85 °C) CO oxidation rate over this catalyst (2.8 mol<sub>CO</sub> h<sup>-1</sup> g<sub>Au</sub><sup>-1</sup>) was almost 30 times higher than that of the Au/Mn<sub>2</sub>O<sub>3</sub>.<sup>108</sup> Qin *et al.*<sup>109</sup> investigated the



toluene oxidation activity over the  $\alpha$ -MnO<sub>2</sub> nanowires supported catalysts with different Ag loading amounts, which greatly affected the toluene oxidation performance. As could be seen in Fig. 8, 4% Ag/MnO<sub>2</sub> catalyst performed the highest activity of the toluene oxidation and the lowest apparent activation energy (45.5 KJ mol<sup>-1</sup>) among Ag/MnO<sub>2</sub> catalysts. They found that 4% loading of Ag could greatly facilitate the adsorption of toluene molecules and optimally increase the activation capacity of MnO<sub>2</sub> lattice oxygen between the interface of Ag and MnO<sub>2</sub>, thereby increasing the reaction rate and promoting deep oxidation between toluene and lattice oxygen.<sup>109</sup> Apart from the loading of noble metals, Sadeghinia *et al.*<sup>84</sup> reported that the catalytic activity of CO oxidation could be enhanced by loading the  $\alpha$ -MnO<sub>2</sub> nanowires with different contents of CuO. The 30% CuO/ $\alpha$ -MnO<sub>2</sub> catalyst could achieve the complete CO conversion at about 100 °C, which was nearly 100 °C lower than pristine  $\alpha$ -MnO<sub>2</sub> nanowire. May *et al.*<sup>69</sup> further confirmed that the loading of CuO by the deposition precipitation (DP) method would make the one-dimensional nanostructure of MnO<sub>2</sub> with more excellent CO catalytic oxidation activity than the incipient wetness impregnation. Specifically, the most active 5CuO/MnO<sub>2</sub> could achieve 80% CO conversion rate at 30 °C.

In view of the excellent performance of CuO loaded MnO<sub>2</sub>-based nanowire catalysts,<sup>84</sup> the researches gradually focused on the transition metals doped catalysts because of the low cost and abundant availability. Lambert *et al.*<sup>110</sup> reported that the catalytic activities of  $\alpha$ -MnO<sub>2</sub> nanowires doped with Cu and Ni

were significantly better than that of the pristine  $\alpha$ -MnO<sub>2</sub> nanowires. Gao *et al.*<sup>61</sup> investigated the effects of doping Fe, Co, Ni, and Cu transition metals on the catalytic performance CO oxidation of  $\alpha$ -MnO<sub>2</sub> 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 MnO<sub>2</sub> nanowires. As could be observed in Fig. 10, the CO oxidation activities of the transition metal doped  $\alpha$ -MnO<sub>2</sub> nanowires were also significantly increased. Among them, Cu doped  $\alpha$ -MnO<sub>2</sub> nanowires showed the best CO oxidation activity. The density functional theory calculations further revealed that doping Cu could more easily form oxygen vacancies in MnO<sub>2</sub> 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 Co<sub>3</sub>O<sub>4</sub>,<sup>111</sup> Cu-doped CeO<sub>2</sub>,<sup>112,113</sup> CuO/Al<sub>2</sub>O<sub>3</sub>.<sup>114</sup> In addition, Jampaiah *et al.*<sup>62</sup> also studied the MnO<sub>2</sub> nanowires doped with two transition metals. Their results showed that the Cu and Co doped MnO<sub>2</sub> nanowires could greatly improve the soot oxidation activity and its T<sub>50</sub> of soot conversion was as low as 279 °C. The advantage of two transition metals doped MnO<sub>2</sub> 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 MnO<sub>2</sub> nanowires. Because the original nanowire morphology would be damaged when the surface metal doping amount reached 20%.<sup>62</sup>

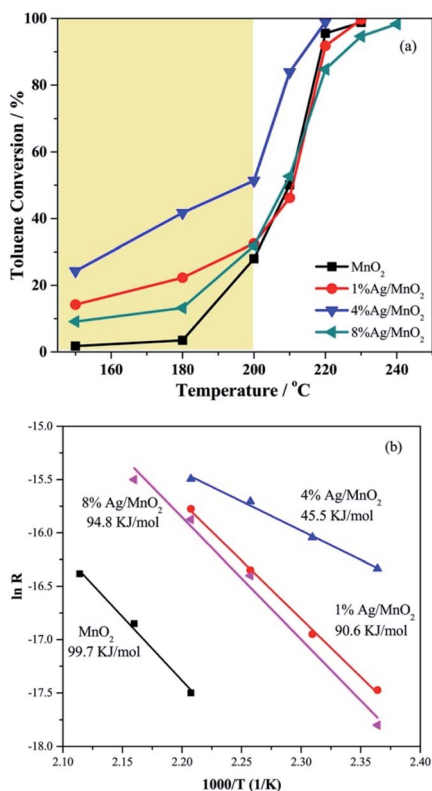


Fig. 8 (a) Catalytic performance of the catalysts for toluene oxidation; (b) Arrhenius plot of the reaction rate of the catalysts. Reproduced by Qin *et al.*<sup>109</sup> with permission from Elsevier.

### 3.5 Interface effect

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

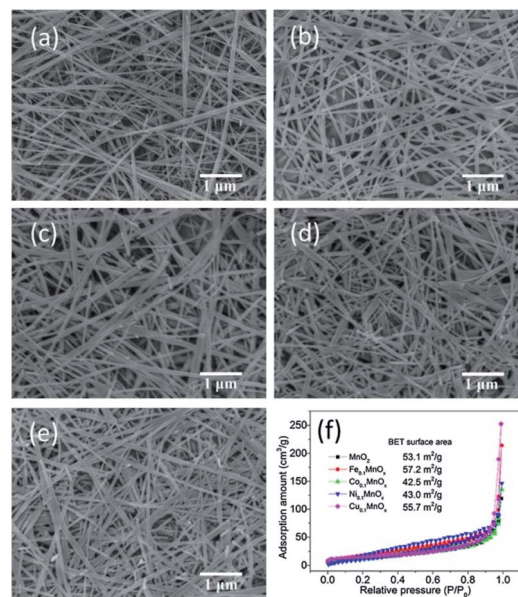


Fig. 9 SEM images of (a) MnO<sub>2</sub>, (b) Fe<sub>0.1</sub>MnO<sub>x</sub>, (c) Co<sub>0.1</sub>MnO<sub>x</sub>, (d) Ni<sub>0.1</sub>MnO<sub>x</sub>, and (e) Cu<sub>0.1</sub>MnO<sub>x</sub> nanowires and (f) N<sub>2</sub> adsorption-desorption isotherms. Reproduced by Gao *et al.*<sup>61</sup> with permission from Elsevier.







Fig. 10 CO oxidation activity tests of the MnO<sub>2</sub> and Fe-, Co-, Ni-, and Cu-doped MnO<sub>2</sub> catalysts. Reproduced by Gao *et al.*<sup>61</sup> with permission from Elsevier.

believed that multi-component metal oxides with coupling interfaces often exhibit better catalytic activity than single-component metal oxides.<sup>115–119</sup> For example, as regards the  $\alpha$ -MnO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> catalyst, the heterogeneous interface constructed by MnO<sub>2</sub> nanowires and Co<sub>3</sub>O<sub>4</sub> nanoparticles could not only enhance the redox pair of Mn<sup>4+</sup>/Mn<sup>3+</sup> and Co<sup>2+</sup>/Co<sup>3+</sup> but also strengthen the adsorption of oxygen on the surface and accelerate the fluidity of oxygen. As a result, the catalytic activities of  $\alpha$ -MnO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> toward the oxidation of benzene<sup>31</sup> and toluene<sup>120</sup> were much better than that of pristine MnO<sub>2</sub> nanowires. The  $\alpha$ -MnO<sub>2</sub> nanowire@Co<sub>3</sub>O<sub>4</sub> could reduce the T<sub>90</sub> of benzene oxidation to 247 °C (see Fig. 11) and the T<sub>90</sub> of toluene conversion to 229 °C, which were 100 °C and 47 °C lower than that of the pure  $\alpha$ -MnO<sub>2</sub> nanowire, respectively.<sup>31,120</sup> Deng *et al.*<sup>121</sup> successfully prepared the MnO<sub>2</sub> nanowire@NiO nanosheet core-shell hybrid nanostructure by uniformly decorating NiO nanosheets on  $\alpha$ -MnO<sub>2</sub> nanowires. The obtained catalyst could achieve the complete oxidation of benzene at 320 °C, which was 60 °C lower than the pure MnO<sub>2</sub> nanowire. Ma *et al.*<sup>122</sup> prepared MnO<sub>2</sub>@TiO<sub>2</sub> by immobilizing crystalline anatase TiO<sub>2</sub> on the surface of  $\alpha$ -MnO<sub>2</sub> nanowire. The as-prepared MnO<sub>2</sub>@TiO<sub>2</sub> exhibited much higher maximum adsorption capacity (105.3 mg g<sup>-1</sup>) of the



Fig. 11 Benzene oxidation activity tests of the 1D MnO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> and 1D MnO<sub>2</sub> catalysts. Reproduced by Tang *et al.*<sup>31</sup> with permission from Elsevier.

radioactive element U(vi) than the pure MnO<sub>2</sub> (13.3 mg g<sup>-1</sup>), illustrating that the performance of the surface-modified MnO<sub>2</sub> was greatly improved.

Homojunctions are junctions layer made of the same semiconductor materials.<sup>44</sup> It has been revealed that the construction of homojunctions could enhance the adsorbing and catalytic performance of the MnO<sub>2</sub> nanomaterials.<sup>123,124</sup> Zhou *et al.*<sup>123</sup> constructed  $\alpha$ -MnO<sub>2</sub>@ $\delta$ -MnO<sub>2</sub> homojunction by loading layered  $\delta$ -MnO<sub>2</sub> nanoflakes on the framework of  $\alpha$ -MnO<sub>2</sub> nanotubes. The  $\alpha$ -MnO<sub>2</sub>@ $\delta$ -MnO<sub>2</sub> homojunction integrated the exposed surfaces of the  $\alpha$ -MnO<sub>2</sub> (100) surface and  $\delta$ -MnO<sub>2</sub> (001) surface at the same time and displayed outstanding catalytic performance toward the oxidation of formaldehyde. The  $\alpha$ -MnO<sub>2</sub> (100) surface was conducive to the adsorption and activation of oxygen molecules and the  $\delta$ -MnO<sub>2</sub> (001) surface was favourable for the desorption of H<sub>2</sub>O. The synergistic effect of the two surfaces significantly enhanced the catalytic activity for formaldehyde oxidation at room temperature. Huang *et al.*<sup>124</sup> synthesized the special two-phase structure MnO<sub>2</sub> catalyst simultaneously with  $\alpha$ -MnO<sub>2</sub> and  $\beta$ -MnO<sub>2</sub> ( $\alpha$ -MnO<sub>2</sub>:  $\beta$ -MnO<sub>2</sub> = 1 : 1). As a result, toluene could be completely oxidized over the  $\alpha$ @ $\beta$ -MnO<sub>2</sub> two-phase catalyst at about 205 °C, which was lower than the pure  $\alpha$ -MnO<sub>2</sub> (220 °C) and  $\beta$ -MnO<sub>2</sub> (260 °C). Compared with the single-phase MnO<sub>2</sub>, the  $\alpha$ @ $\beta$ -MnO<sub>2</sub> 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<sub>2</sub>.<sup>125</sup> 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

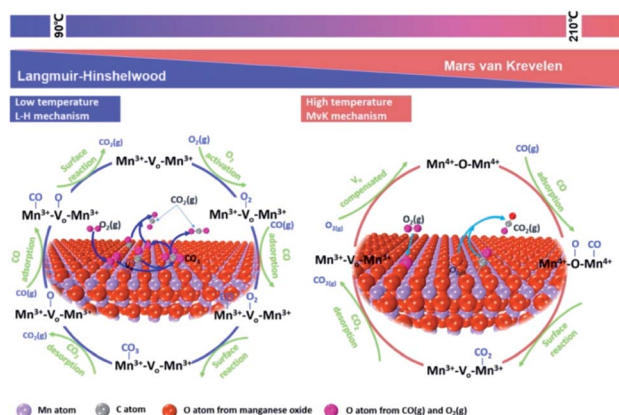


Fig. 12 Proposed reaction mechanism of CO oxidation on metal oxide. Reproduced by Tian *et al.*<sup>126</sup> with permission from Elsevier.



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).<sup>126</sup> When the temperature is low (50–90 °C), gaseous O<sub>2</sub> are captured by oxygen vacancies and the active oxygen species (O<sub>2</sub><sup>-</sup> or O<sub>2</sub><sup>2-</sup>) could be formed. Subsequently, the adsorbed CO (CO–Mn<sup>3+</sup>) tent reacts with active oxygen species to generate bidentate carbonate species, and then decompose into CO<sub>2</sub>. Finally, the dissociated O species could be restrained by oxygen vacancies and react with the adsorbed CO to form CO<sub>2</sub> which follows the L–H mechanism. When the temperature is high ( $T > 190$  °C), the surface lattice oxygen species can directly react with adsorbed CO to generate CO<sub>2</sub> and oxygen vacancies due to the activation of surface lattice oxygen species. Subsequently, the oxygen vacancy was refilled by gaseous O<sub>2</sub> and the redox cycle is completed by following the MvK mechanism. The T<sub>10</sub>, T<sub>50</sub>, T<sub>90</sub>, T<sub>100</sub> and BET of

MnO<sub>2</sub>-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 MnO<sub>2</sub>.<sup>26,92,127</sup> Liang *et al.*<sup>26</sup> synthesized four different crystalline MnO<sub>2</sub> nano-oxides. They found that the order of activity for catalytic oxidation of CO was  $\alpha \approx \delta > \gamma > \beta$ -MnO<sub>2</sub>. Because the tunnel structure of [2 × 2] and [1 × 1] of  $\alpha$ -MnO<sub>2</sub> could occupy more space to obtain more CO adsorption sites; whereas, other crystalline MnO<sub>2</sub> only involved  $\beta$ -MnO<sub>2</sub> with [1 × 1] tunnel,  $\gamma$ -MnO<sub>2</sub> with [2 × 1] and [1 × 1] tunnels, and  $\delta$ -MnO<sub>2</sub> composed of [MnO<sub>6</sub>] octahedrons shared by the double-layer edges. Another reason accounting for the enhanced catalytic CO oxidation performance of  $\alpha$ -MnO<sub>2</sub> was that the elongated Mn–O bond length stemming from the distorted [MnO<sub>6</sub>] units could benefit the cracking of the Mn–O bond, promoting CO oxidation.<sup>26,127</sup> As a result,  $\alpha$ -MnO<sub>2</sub> could easily react with CO and thus further improved its catalytic performance.

Table 2 T<sub>10</sub>, T<sub>50</sub>, T<sub>90</sub>, and T<sub>100</sub> of MnO<sub>2</sub>-based nanowire catalysts toward different catalytic substances

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



In addition, various studies have been conducted to improve the catalytic activity of MnO<sub>2</sub>-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.*<sup>61</sup> found that the hydrothermal doping of Cu would significantly increase CO oxidation activity (TOF =  $9.1 \times 10^{-3} \text{ s}^{-1}$  at 70 °C) and water resistance of  $\alpha$ -MnO<sub>2</sub> nanowires. As for  $\gamma$ -MnO<sub>2</sub>, Zn-doped MnO<sub>2</sub> 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  $\gamma$ -MnO<sub>2</sub>.<sup>128</sup> Besides, the surface engineering is considered as another effective method to improve the catalytic activity of MnO<sub>2</sub>. Li *et al.*<sup>92</sup> synthesized  $\alpha$ -MnO<sub>2</sub> with a large number of surface open cells through acid treatment. The open cells were rich in adsorption sites for O<sub>2</sub>, thus enhancing the catalytic activity of MnO<sub>2</sub> for CO oxidation. Moreover, combining Au,<sup>56</sup> Ag,<sup>127</sup> CuO,<sup>69,84</sup> *etc.* with MnO<sub>2</sub> nanomaterials can effectively improve CO oxidation efficiency. Xu *et al.*<sup>127</sup> investigated the CO oxidation activity over the  $\alpha$ -MnO<sub>2</sub> nanowires supported Ag based catalysts and the T<sub>90</sub> of Ag/ $\alpha$ -MnO<sub>2</sub> below 100 °C could be achieved. Although many studies have been carried out to enhance the catalytic activity of MnO<sub>2</sub> for CO oxidation and the complete CO conversion could be achieved at -34 °C,<sup>56</sup> 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.<sup>129</sup> Besides, most VOCs emitted into the atmosphere can cause the formation of secondary pollutants, such as tropospheric ozone, peroxyacetyl nitrate, and secondary organic aerosols.<sup>130-132</sup> Various means have been used to remove the VOCs, such as the physical adsorption,<sup>133</sup> catalytic oxidation,<sup>134,135</sup> photocatalytic degradation,<sup>136,137</sup> plasma catalytic oxidation,<sup>138</sup> and biological decomposition.<sup>139</sup> 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.<sup>140</sup> MnO<sub>2</sub> 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.<sup>141</sup>

**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.<sup>129</sup> Up to now, the supported noble metal based catalysts, such as Pt, Pd, Au,

Ag based catalysts,<sup>142-145</sup> 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 MnO<sub>2</sub> based catalysts are promising candidates due to facile availability.

Hu *et al.*<sup>146</sup> found that the order of catalytic activities on benzene combustion over MnO<sub>2</sub> with different phase structures was  $\gamma$ -MnO<sub>2</sub> >  $\beta$ -MnO<sub>2</sub> >  $\alpha$ -MnO<sub>2</sub> >  $\delta$ -MnO<sub>2</sub>. The surface adsorbed oxygen species concentration and low temperature O<sub>2</sub> 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 MnO<sub>2</sub>. Liu *et al.*<sup>147</sup> found that the Ce<sup>3+</sup> and Cu<sup>2+</sup> doped of MnO<sub>2</sub> nanosheet could significantly improve the activity of MnO<sub>2</sub> for benzene decomposition. For the pristine MnO<sub>2</sub>, benzene was hardly decomposed below 200 °C and only ~40% conversion was achieved at 400 °C. Whereas, as for the Ce-MnO<sub>2</sub> and Cu-MnO<sub>2</sub> catalysts, the benzene started to decompose around 100 °C and nearly all benzene could be removed around 250 °C. Moreover, the Cu-MnO<sub>2</sub> catalyst also exhibited high resistance to high-temperature deactivation and water resistance during continuous long-term testing. Recently, Ma *et al.*<sup>148</sup> synthesized the tungsten-doped MnO<sub>2</sub> (W-MnO<sub>2</sub>) 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 MnO<sub>2</sub>, but also produce strong covalent interactions with adjacent O atoms through W-O bridge bonds, thereby promoting O<sub>2</sub> polarization and electron transference.

As for the metal loading, Ye *et al.*<sup>149</sup> prepared nanosized  $\alpha$ -MnO<sub>2</sub>-supported silver catalysts for benzene oxidation. They found that the 5Ag/MnO<sub>2</sub> catalyst performed the best activity of the benzene oxidation. Tang *et al.*<sup>31</sup> modified one-dimensional MnO<sub>2</sub>-based catalysts (wire-like, rod-like  $\alpha$ -MnO<sub>2</sub> and  $\beta$ -MnO<sub>2</sub> microrods) by the Co<sub>3</sub>O<sub>4</sub> nanoparticles (see Fig. 13) and investigated them as the catalysts for benzene oxidation. They found that the modified MnO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> composite exhibited better catalytic performance than the pristine MnO<sub>2</sub>. The specific conversion efficiencies of the modified material to benzene abided by the order of  $\alpha$ -MnO<sub>2</sub> nanowires >  $\alpha$ -MnO<sub>2</sub> nanorods >  $\beta$ -MnO<sub>2</sub> 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 MnO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> hetero-nanostructures. Reproduced by Tang *et al.*<sup>31</sup> with permission from Elsevier.





**4.2.2 Toluene.** Toluene could directly threaten the human health and safety because of its carcinogenicity and teratogenicity.<sup>150,151</sup> 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.*<sup>83</sup> found that  $\alpha$ -MnO<sub>2</sub> nanowires performed much higher catalytic activity than the commercial MnO<sub>2</sub> counterpart toward toluene combustion. The reason for this could be attributed to the enhanced surface oxygen mobility and surface area of  $\alpha$ -MnO<sub>2</sub> nanowires, which were significantly better than the commercial MnO<sub>2</sub>. The possible oxidation reaction mechanism of toluene over  $\alpha$ -MnO<sub>2</sub> catalyst was summarized in Fig. 14. Firstly, toluene adsorbed on  $\alpha$ -MnO<sub>2</sub> 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 O<sub>2</sub>, and active oxygen species (O<sub>2</sub>/O<sub>2</sub><sup>-</sup>/O<sub>2</sub><sup>2-</sup>/O<sup>-</sup>/O<sup>2-</sup>) would be formed.<sup>86</sup> 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 unsaturated long chain enol and alkyne could be ultimately transformed into the CO<sub>2</sub> and H<sub>2</sub>O quickly.<sup>87</sup>

It has been reported that the catalytic performances of the toluene oxidation over the MnO<sub>2</sub> nanomaterials were strongly related to the crystalline phase structures.<sup>91,124,152</sup> Li *et al.*<sup>91</sup> prepared MnO<sub>2</sub> with different crystalline phases ( $\beta$ -,  $\alpha$ -,  $\gamma$ -, and  $\delta$ -). The results showed that catalytic toluene oxidation activities followed the sequence of  $\delta > \gamma > \alpha > \beta$ -MnO<sub>2</sub>. The morphology of the MnO<sub>2</sub> nanostructure also greatly influences the catalytic performance of the toluene oxidation. The previous study showed that the MnO<sub>2</sub> nanowire showed the most excellent toluene combustion catalytic activity (T<sub>100</sub> = 220 °C) after loading silver among the MnO<sub>2</sub>-based one-dimensional nanostructures (nanowire, nanorod, and nanotube).<sup>30</sup>

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

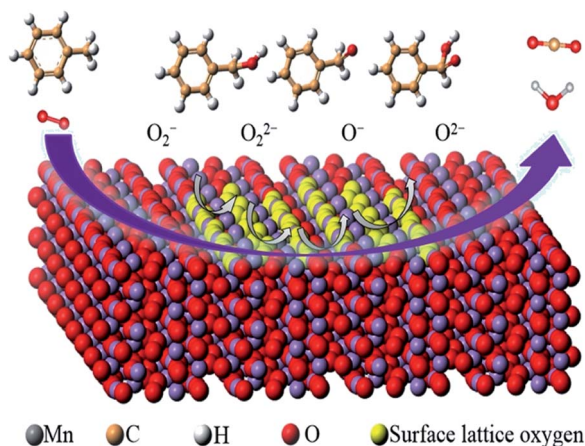


Fig. 14 Proposed mechanism of toluene degradation pathway on  $\alpha$ -MnO<sub>2</sub>. Reproduced by Huang *et al.*<sup>87</sup> with permission from Elsevier.

Ca<sup>2+</sup> into MnO<sub>2</sub> promised the higher catalytic activity for toluene oxidation than pristine MnO<sub>2</sub>. Specifically, the Ca-MnO<sub>2</sub> catalyst exhibited the best catalytic activity (T<sub>90</sub> = 215 °C) and possessed good water resistance. The outstanding catalytic performance of Ca-MnO<sub>2</sub> was closely related to the abundant acidic sites, high oxygen vacancy concentration, and the weak CO<sub>2</sub> adsorption capacity. Min *et al.*<sup>154</sup> found that transition metal (Ni and Co) doped  $\alpha$ -MnO<sub>2</sub> and  $\beta$ -MnO<sub>2</sub> 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  $\alpha$ -MnO<sub>2</sub> and  $\beta$ -MnO<sub>2</sub>.

The catalytic performance of the toluene oxidation was also influenced by the interface between different metal oxides. Ren *et al.*<sup>120</sup> fabricated ZIF-derived Co<sub>3</sub>O<sub>4</sub> grown *in situ* on 1D  $\alpha$ -MnO<sub>2</sub> materials (as displayed in Fig. 15) and used it as the catalyst for toluene oxidation. They found that the  $\alpha$ -MnO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> could reduce the T<sub>90</sub> of toluene conversion to 229 °C, which was 47 °C and 28 °C lower than those of the pure  $\alpha$ -MnO<sub>2</sub> nanowire and Co<sub>3</sub>O<sub>4</sub>-b, respectively. The main reason for the enhanced catalytic activity could be attributed to the synergistic effect produced by the coupling interface constructed between  $\alpha$ -MnO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub>. The specific reaction route of toluene oxidation on  $\alpha$ -MnO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> catalyst could be illustrated as follows: toluene → benzoate species → alkanes containing oxygen functional group → CO<sub>2</sub> and H<sub>2</sub>O. In addition, the  $\alpha$ -MnO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> catalyst also exhibited excellent stability and water resistance during the toluene oxidation.<sup>120</sup> Zhang *et al.*<sup>155</sup> found that the fluorine (F)-doped titanium dioxide (TiO<sub>2</sub>) coupled with a small number of  $\alpha$ -MnO<sub>2</sub> 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 exists in the industrial wastewater, such as petroleum refinery, wood preservation, and coking.<sup>156</sup> Phenol is a highly toxic substance, which has been listed as one of the most important organic pollutants with carcinogenic, mutagenic, and teratogenic hazards.<sup>157</sup> Although MnO<sub>2</sub>-based nanowires have been widely used in environmental catalysis, yet there are few studies investigating the application of MnO<sub>2</sub>-based nanowire materials in water treatment. Dong *et al.*<sup>158</sup> found out that

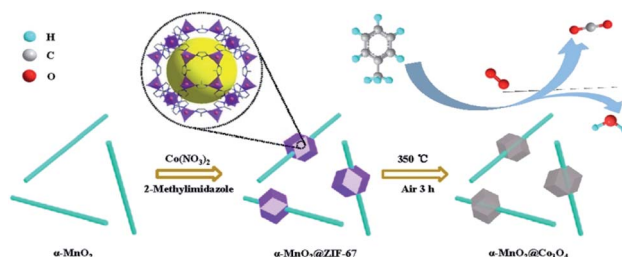


Fig. 15 Illustration of the fabrication of  $\alpha$ -MnO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub> samples. Reproduced by Ren *et al.*<sup>120</sup> with permission from Elsevier.



the  $\beta$ - $\text{MnO}_2$  nanowires possessed outstanding catalytic performance for phenol degradation. Saputra *et al.*<sup>159</sup> found that the  $\alpha$ - $\text{MnO}_2$  materials exhibited different activities in activating peroxydisulfate to produce sulfate radicals for phenol degradation because of the variety in the phase structure and morphology. The results demonstrated that  $\alpha$ - $\text{MnO}_2$  nanowire presented the highest activity with stable performance among the investigated nanomaterials. Then, they investigated the effect of phase structure of  $\text{MnO}_2$ -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  $\alpha$ - $\text{MnO}_2$  still exhibited higher activity than the rod-like  $\beta$ - $\text{MnO}_2$  and fiber-like  $\gamma$ - $\text{MnO}_2$  because of the large specific surface area and unique tunnel structure. Besides, the  $\beta$ - $\text{MnO}_2$  exhibited the lowest activity due to single tunnel and stable oxygen reducibility. Meanwhile, Peng *et al.*<sup>160</sup> also illustrated that  $\alpha$ - $\text{MnO}_2$  nanowires performed higher activity than  $\alpha$ - $\text{MnO}_2$  nanotubes in the catalytic phenol degradation. The probable reason for this was that  $\alpha$ - $\text{MnO}_2$  nanowire possessed much greater surface area and lower negative surface charge density than the  $\alpha$ - $\text{MnO}_2$  nanotube, further accounting for the higher catalytic activities. Liang *et al.*<sup>161</sup> synthesized the mesoporous  $\text{Co}_3\text{O}_4/\alpha$ - $\text{MnO}_2$  catalyst exhibiting greatly high activity in peroxydisulfate activation for phenol degradation with 100% conversion in 20 min. The stability tests also showed that the mesoporous  $\text{Co}_3\text{O}_4/\text{MnO}_2$  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.<sup>162–164</sup> 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

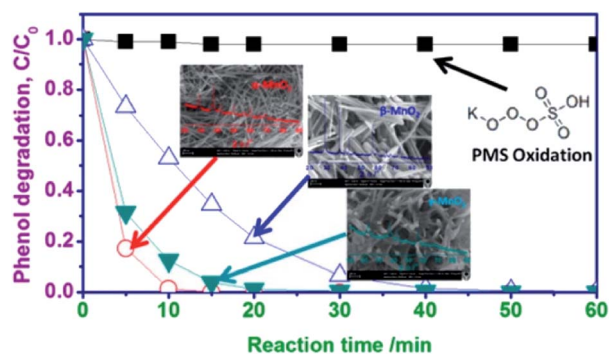


Fig. 16 Phenol degradation of  $\text{MnO}_2$ -based nanomaterials with different phase structures. Reproduced by Saputra *et al.*<sup>29</sup> with permission from ACS.

contain platinum.<sup>165–167</sup> Therefore, their widely industrial and commercial applications are severely restricted because of the high cost. Sekine *et al.*<sup>168</sup> found that  $\text{MnO}_2$  could react with HCHO and release  $\text{CO}_2$  even at room temperature. This indicated that  $\text{MnO}_2$  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.*<sup>169</sup> proposed a possible HCHO oxidation mechanism over the partially crystallized mesoporous  $\text{MnO}_x$  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:  $\text{O}_{\text{ads}}$ ); Secondly,  $\text{Mn}^{3+}$  is oxidized into  $\text{Mn}^{4+}$  by  $\text{O}_{\text{ads}}$  and meanwhile one electron is released to  $\text{O}_{\text{ads}}$  to produce  $\text{O}^-$ .<sup>170,171</sup> Thirdly, the adsorbed HCHO on the surface of manganese oxide is oxidized into the HCOOH intermediate by the  $\text{O}^-$ . During this process, an electron will transfer from  $\text{O}^-$  to manganese cations and reduce  $\text{Mn}^{4+}$  to  $\text{Mn}^{3+}$  at the same time. Subsequently, the HCOOH intermediate further decomposes into  $\text{H}^+$  and  $\text{HCOO}^-$ .<sup>168,172</sup> The  $\text{HCOO}^-$  subsequently reacts with another  $\text{O}_{\text{ads}}$  to produce  $\text{HCO}_3^-$  and  $\text{HCO}_3^-$  is finally degraded into  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .

Li *et al.*<sup>174</sup> reported that the sphere-like mesoporous  $\text{MnO}_2$  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.*<sup>94</sup> studied the catalytic activity of formaldehyde oxidation over the  $\text{MnO}_2$  nanomaterials with different phase structures ( $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -). It was found that the  $\delta$ - $\text{MnO}_2$  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  $\alpha$ -,  $\beta$ -, and  $\gamma$ - $\text{MnO}_2$  at 125 °C, 200 °C, 150 °C, respectively. Besides, previous researches revealed that the Au-doped<sup>175</sup> and Ag-loading<sup>176</sup>  $\alpha$ - $\text{MnO}_2$  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  $\alpha$ - $\text{MnO}_2$  nanorods, respectively. Rong *et al.*<sup>86</sup> prepared (310) facet

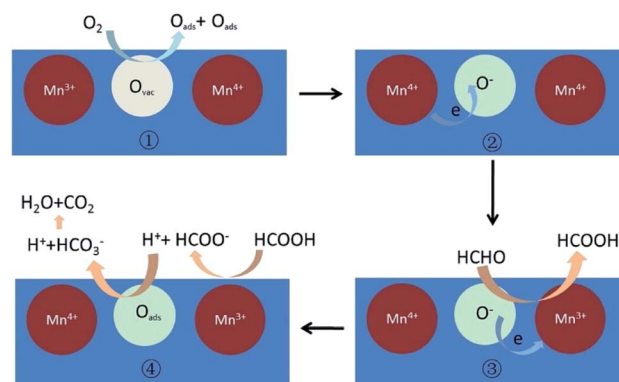


Fig. 17 The possible mechanism of catalytic oxidation of HCHO to  $\text{CO}_2$  on partially crystallized mesoporous  $\text{MnO}_x$  under dry condition. Reproduced by Guan *et al.*<sup>173</sup> with permission from Elsevier.



exposed  $\alpha$ -MnO<sub>2</sub> nanowire catalyst through crystal facet engineering with superior HCHO oxidation activity. It could completely convert HCHO into CO<sub>2</sub> at 60 °C and achieve 86% conversion rate of 0.53 mg m<sup>-3</sup> HCHO at room temperature. He *et al.*<sup>177</sup> enhanced the catalytic oxidation of HCHO at ambient temperature over the  $\alpha$ -MnO<sub>2</sub> with four well-defined morphologies (nanowire, nanotube, nanorod, and nanoflower) with the help of the mechanical vibration. Among them,  $\alpha$ -MnO<sub>2</sub> 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 (CH<sub>3</sub>SH) is a highly toxic and corrosive sulfur-containing VOC (S-VOCs). It is widely released from sewage treatment and sanitary landfill.<sup>178</sup> The exposure of CH<sub>3</sub>SH at few ppm-level can make the human feel unpleasant and dozens of ppm-level can cause significant poisoning.<sup>179,180</sup> In these years, the catalytic removal of CH<sub>3</sub>SH has been extensively studied. Catalytic combustion technology is considered as one of the most efficient technologies to convert S-VOCs into less toxic products (CO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>, *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.<sup>181–185</sup> 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.<sup>186,187</sup> In most studies, supported noble metals (Au, Ag, Pt and Pd, *etc.*) and low-cost metal oxides like NiO, Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub>, MnO<sub>x</sub>, and Co<sub>3</sub>O<sub>4</sub> have been developed as efficient catalysts for the catalytic ozonation of S-VOCs.<sup>187</sup> MnO<sub>2</sub> is the most widely studied due to its plentiful valence states, versatile structures, high stability, and low cost.

The oxygen vacancies in MnO<sub>2</sub> are usually considered as the active sites for O<sub>3</sub> adsorption and catalysing ozonation.<sup>188</sup> Fig. 18 shows the adsorption of CH<sub>3</sub>SH over the MnO<sub>2</sub> catalyst and the mechanism of catalytic ozone.<sup>93</sup> O<sub>3</sub> can be captured and decomposed by the structural defects on the MnO<sub>2</sub> surface, then transformed into activate oxygen species (O<sup>2-</sup>/O<sub>2</sub><sup>2-</sup>), and quickly evolved into <sup>•</sup>O<sub>2</sub><sup>-</sup>/<sup>•</sup>OH/<sup>1</sup>O<sub>2</sub> through a chain cycle reaction, which can directly participate in CH<sub>3</sub>SH and adsorbed CH<sub>3</sub>S<sup>-</sup> 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.*<sup>93</sup> prepared  $\alpha$ -MnO<sub>2</sub> nanowire with different crystal facets exposed and successfully employed them to catalyse the ozonation of CH<sub>3</sub>SH. The synthesized 310-MnO<sub>2</sub> catalyst performed higher activity than the 110-MnO<sub>2</sub> and 100-MnO<sub>2</sub>. In addition, previous researches found that loading the metal active sites on MnO<sub>2</sub> nanomaterials could also enhance the ozonation catalysis of CH<sub>3</sub>SH.<sup>187,189</sup> Xia *et al.*<sup>187</sup> prepared Ag deposited three-dimensional MnO<sub>2</sub> porous hollow microspheres (Ag/MnO<sub>2</sub> PHMSs). The optimal 0.3% Ag/MnO<sub>2</sub> PHMSs could completely degrade 70 ppm CH<sub>3</sub>SH within 600 seconds, displaying much higher efficiency than that of the pristine MnO<sub>2</sub> PHMSs support (79%). Additionally, the catalyst retained long-term stability and could be facily regenerated to its initial activity with ethanol and HCl. Yang *et al.*<sup>189</sup> synthesized urchin-like oxygen vacancy-rich (V<sub>O</sub>) hollow-structured MnO<sub>2</sub> with the loading of CuO

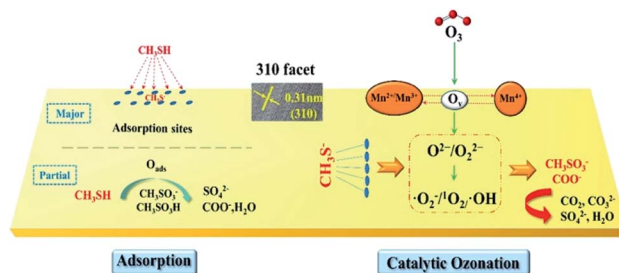


Fig. 18 Mechanism of adsorption and catalytic ozonation toward CH<sub>3</sub>SH by 310- $\alpha$ -MnO<sub>2</sub> catalysts. Reproduced by He *et al.*<sup>93</sup> with permission from ACS.

nanoparticles on the surface (CuO/V<sub>O</sub>-MnO<sub>2</sub>). The well-dispersed CuO on the surface of urchin-like hollow MnO<sub>2</sub> enhanced the chemisorption of CH<sub>3</sub>SH, thus promoting the efficient decomposition of CH<sub>3</sub>SH on the CuO/V<sub>O</sub>-MnO<sub>2</sub>. Among the as-prepared CuO/V<sub>O</sub>-MnO<sub>2</sub> catalyst, the 5CuO/V<sub>O</sub>-MnO<sub>2</sub> realized the optimum CH<sub>3</sub>SH removal efficiency (98.5%) within 1200 s reaction under 25 °C, which was obviously higher than that of individual MnO<sub>2</sub> (70.7%) and CuO (57.0%).

However, there are few researches about the wire-like MnO<sub>2</sub> for the ozonation of CH<sub>3</sub>SH except for the study of He.<sup>93</sup> In view of the strong interaction between wire-like MnO<sub>2</sub> and noble/transition metals, more attentions will be attributed to the metal loading/doping of MnO<sub>2</sub> nanowire for the ozonation of CH<sub>3</sub>SH in the future research.

### 4.3 Ozone

Ozone (O<sub>3</sub>) is a light blue gas with special odor and strong oxidizing ability. O<sub>3</sub> 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.<sup>190–193</sup> The catalysts used for the degradation of ozone can be divided into noble metals,<sup>194,195</sup> transition metal oxides<sup>196–201</sup> and noble transition compounds.<sup>202</sup> 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 MnO<sub>2</sub>.

$\alpha$ -MnO<sub>2</sub> is a newly emerging material for catalytic decomposition of ozone. Jia *et al.*<sup>141</sup> investigated the ozone removal activity over the MnO<sub>2</sub> with different phase structures ( $\alpha$ ,  $\beta$ , and  $\gamma$ ). They found that  $\alpha$ -MnO<sub>2</sub> performed the highest ozone removal efficiency. Zhu *et al.*<sup>203</sup> developed a hierarchical structure consisted of graphene encapsulating  $\alpha$ -MnO<sub>2</sub> 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





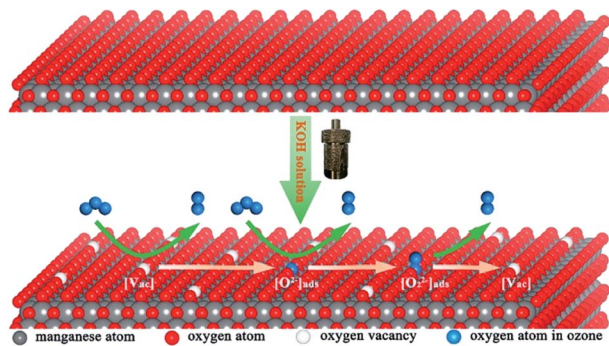


Fig. 19 Schematic of ozone catalytic decomposition on the K-rich  $\text{MnO}_2$ . Reproduced by Zhu *et al.*<sup>82</sup> with permission from ACS.

could reach 70%, well beyond the performance of  $\alpha$ - $\text{MnO}_2$  nanofiber. Zhang *et al.*<sup>155</sup> found that introducing  $\alpha$ - $\text{MnO}_2$  nanowires into the fluorine (F)-doped titanium dioxide ( $\text{TiO}_2$ ) could not only improve the photocatalytic degradation of toluene but also remove almost the total  $\text{O}_3$  in the system. As the comparison, only 15.8% of  $\text{O}_3$  could be removed by the pristine F- $\text{TiO}_2$  catalyst without mixing with  $\alpha$ - $\text{MnO}_2$ . This indicated that  $\alpha$ - $\text{MnO}_2$  nanowire was an excellent catalyst for  $\text{O}_3$  decomposition. Previous study showed that the oxygen vacancies on  $\text{MnO}_2$  nanomaterials were active sites for ozone adsorption and further decomposition,<sup>199</sup> which largely determined the catalytic degradation activity of  $\text{MnO}_2$ . Zhu *et al.*<sup>82</sup> developed the  $\alpha$ - $\text{MnO}_2$  nanowire with high  $\text{K}^+$  content in tunnel structure through the simple KOH solution post-treatment. As shown in Fig. 19, the substantial increase in  $\text{K}^+$  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  $\text{K}^+$ . However, peroxide species ( $\text{O}_2^{2-}$ ) 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.*<sup>204</sup> prepared cerium-modified todorokite-type manganese dioxides ( $\text{Ce-MnO}_2$ ). The as-obtained catalyst showed greatly improved stability, which could keep  $\sim 98\%$  of removal efficiency for  $\sim 115$  ppm of  $\text{O}_3$  within 5 h under a very high space velocity of  $1200 \text{ L g}^{-1} \text{ h}^{-1}$  at room temperature. Besides, the  $\text{Ce-MnO}_2$  catalyst also exhibited highly stable  $\text{O}_3$  removal efficiency at temperature as low as  $0^\circ\text{C}$ .

## 5. Summary and prospect

$\text{MnO}_2$ -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  $\text{MnO}_2$ -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  $\text{O}_3$ .

(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  $\text{MnO}_2$  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  $\text{MnO}_2$ -based nanomaterials. Therefore, it is often used in combination with template method to prepare highly ordered  $\text{MnO}_2$  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  $\text{MnO}_2$  nanowires. Compared with the influences of phase structure and morphology, it has more significant impact on the catalytic activity of  $\text{MnO}_2$  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  $\text{MnO}_2$  nanowires. As a result, the catalytic performance will be improved by increasing the fluidity of oxygen.

Up to now, lots of  $\text{MnO}_2$ -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  $\text{MnO}_2$ -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  $\text{MnO}_2$  result in challenging obstacles in obtaining pure phase structures and uniform morphologies of  $\text{MnO}_2$  nanowires. Therefore, it is urgent to develop stable and efficient strategies to fabricate  $\text{MnO}_2$  nanowires in single-crystalline solids with uniform morphology. Considering the remarkable improvement of the catalytic oxidation ability of  $\text{MnO}_2$  nanowire by the crystal facet engineering, novel synthesis strategies for  $\text{MnO}_2$  nanowire exposed a high proportion of specific crystal facet should be investigated in depth.

(2) The crystal facet engineering of  $\text{MnO}_2$  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  $\text{MnO}_2$ , 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  $\text{MnO}_2$  nanowire by loading or doping rare earth metals (La, Ce, Pr, and Sm). In view of the improvement of the  $\text{O}_3$  removal



efficiency of MnO<sub>2</sub> 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 MnO<sub>2</sub>-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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