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Spontaneous generation of singlet oxygen on microemulsion-derived manganese oxides with rich oxygen vacancies for efficient aerobic oxidation

$N_{55}$ - $MnO_2$  nanocatalysts with oxygen vacancy concentrations as high as 51.1% can be obtained by strategically incorporating defect engineering and interstitial N using compartmentalized-microemulsion crystallization followed by post-calcination. This feature allows the nanocatalyst to expose a substantial number of  $O_v$  and interstitial N sites on the surface of  $N_{55}$ - $MnO_2$ , facilitating effective chemisorption and activation of  $O_2$ . As a result, the  $N_{55}$ - $MnO_2$  nanocatalyst enables room-temperature aerobic oxidation of alcohols with a yield surpassing 99%, representing a 6.7-fold activity enhancement compared to  $\epsilon$ - $MnO_2$  without N-doping.

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# Spontaneous generation of singlet oxygen on microemulsion-derived manganese oxides with rich oxygen vacancies for efficient aerobic oxidation†

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Developing innovative catalysts for efficiently activating O<sub>2</sub> into singlet oxygen (<sup>1</sup>O<sub>2</sub>) is a cutting-edge field with the potential to revolutionize green chemical synthesis. Despite its potential, practical implementation remains a significant challenge. In this study, we design a series of nitrogen (N)-doped manganese oxides (N<sub>y</sub>-MnO<sub>2</sub>, where y represents the molar amount of the N precursor used) nanocatalysts using compartmentalized-microemulsion crystallization followed by post-calcination. These nanocatalysts demonstrate the remarkable ability to directly produce <sup>1</sup>O<sub>2</sub> at room temperature without the external fields. By strategically incorporating defect engineering and interstitial N, the concentration of surface oxygen atoms (O<sub>s</sub>) in the vicinity of oxygen vacancy (O<sub>v</sub>) reaches 51.1% for the N<sub>55</sub>-MnO<sub>2</sub> nanocatalyst. This feature allows the nanocatalyst to expose a substantial number of O<sub>v</sub> and interstitial N sites on the surface of N<sub>55</sub>-MnO<sub>2</sub>, facilitating effective chemisorption and activation of O<sub>2</sub>. Verified through electron paramagnetic resonance spectroscopy and reactive oxygen species trapping experiments, the spontaneous generation of <sup>1</sup>O<sub>2</sub>, even in the absence of light, underscores its crucial role in aerobic oxidation. Density functional theory calculations reveal that an increased O<sub>v</sub> content and N doping significantly reduce the adsorption energy, thereby promoting chemisorption and excitation of O<sub>2</sub>. Consequently, the optimized N<sub>55</sub>-MnO<sub>2</sub> nanocatalyst enables room-temperature aerobic oxidation of alcohols with a yield surpassing 99%, representing a 6.7-fold activity enhancement compared to ε-MnO<sub>2</sub> without N-doping. Furthermore, N<sub>55</sub>-MnO<sub>2</sub> demonstrates exceptional recyclability for the aerobic oxidative conversion of benzyl alcohol over ten cycles. This study introduces an approach to spontaneously activate O<sub>2</sub> for the green synthesis of fine chemicals.

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## Introduction

Singlet oxygen (<sup>1</sup>O<sub>2</sub>), recognized as a highly active and environmentally friendly reactive oxygen species (ROS), has garnered substantial attention from researchers in recent years.<sup>1-4</sup> Benefiting from its remarkable oxidative capabilities and eco-friendliness, <sup>1</sup>O<sub>2</sub> has found widespread applications in green catalysis,<sup>5-7</sup> photocatalytic degradation,<sup>8</sup> tumor diagnosis and treatment,<sup>9</sup> and fluorescence probes.<sup>10</sup> Nevertheless, the practical generation of <sup>1</sup>O<sub>2</sub> typically necessitates intense photoexcitation due to the spin transition between ground and excited state molecular oxygen.<sup>11</sup> Throughout the last few decades, a range of photosensitizers, including photosensitive organic dyes,<sup>12</sup> organometallic complexes,<sup>13</sup> and noble metals,<sup>14,15</sup> have been devised to produce <sup>1</sup>O<sub>2</sub> by harnessing photogenerated excitons and energy transfer pathways. However, the scarcity of noble metals and the susceptibility of organic photosensitizers to degradation render them inadequate to fulfill the escalating



needs of green chemistry and sustainable development.<sup>11,16</sup> Therefore, the construction of cost-effective and stable triggers for self-activating O<sub>2</sub> in a mild environment through catalyst innovation holds great significance.

Transition metal oxides are being considered as suitable candidates to replace noble metal catalysts due to their significant advantages, including low cost, excellent stability, and abundant reserves.<sup>17–20</sup> Among these, manganese dioxides (MnO<sub>2</sub>) stand out due to the multiple valence states and intricate electronic structures, which can be readily modified through structural-tailoring strategies to enhance their redox capabilities. Our previous studies have demonstrated the effectiveness of *in situ* heteroatom insertion techniques in producing highly active catalysts with ample oxygen vacancies (O<sub>v</sub>).<sup>17,19</sup> These O<sub>v</sub> play a pivotal role in promoting the mobility of lattice oxygen (O<sub>l</sub>), consequently enhancing oxidative capability through the Mars–Van Krevelen (MVK) mechanism, rather than inducing spontaneous O<sub>2</sub> transformation into <sup>1</sup>O<sub>2</sub>.<sup>21</sup> While theoretical studies have suggested that O<sub>2</sub> adsorbed on the surface of metal oxides can lead to the direct generation of <sup>1</sup>O<sub>2</sub>, experimental breakthroughs in this area have been limited.<sup>22–24</sup> Fortunately, the defect-engineering approach, particularly by modulating rich O<sub>v</sub>, promotes the chemisorption of O<sub>2</sub>, offering a promising avenue for activating O<sub>2</sub> to form ROS.<sup>25–31</sup> For instance, the {111} facet of MgO, with its abundance of O<sub>v</sub>, enables chemisorbed O<sub>2</sub> to undergo molecule transitions and electron rearrangements, resulting in the production of <sup>1</sup>O<sub>2</sub> even in the absence of light. However, the application in catalysis remains rarely explored.<sup>24</sup> It can be inferred that an increase in O<sub>v</sub> content facilitates O<sub>2</sub> chemisorption on the surface of the catalyst, thereby promoting the formation of <sup>1</sup>O<sub>2</sub>.<sup>24,25</sup> These inspire us to devise catalysts with enhanced activity by creating ample surface chemisorption sites through innovative defect-engineering strategies.

The microemulsion composed of immiscible oleic and aqueous phases serves as a versatile platform for fabricating various nanocatalysts, distinguishing it significantly from conventional methods.<sup>32,33</sup> Additionally, the utilization of microemulsions as templates for MnO<sub>2</sub> preparation offers unique advantages: (1) confined aqueous microdroplets create a conducive environment for effective heteroatom doping and the formation of abundant O<sub>v</sub>; (2) uniformly sized MnO<sub>2</sub> nanocatalysts formed within these microdroplets tend to expose a higher proportion of surface O<sub>v</sub>.<sup>32,33</sup> However, the strategy of

constructing high-concentration O<sub>v</sub> based on a microemulsion microreactor is rarely reported.<sup>25</sup>

In this study, we synthesized N-doped MnO<sub>2</sub> (N<sub>y</sub>-MnO<sub>2</sub>, where y represents the molar amount of urea used) nanocatalysts with adjustable O<sub>v</sub> through crystallization within compartmentalized droplets of a microemulsion, followed by calcination. The resulting N<sub>y</sub>-MnO<sub>2</sub> nanocatalysts are employed to activate O<sub>2</sub> and generate <sup>1</sup>O<sub>2</sub> for green oxidation processes. As demonstrated in the aerobic oxidation of benzyl alcohol, an important reaction pathway for the synthesis of fine chemicals, the catalytic activity of N<sub>55</sub>-MnO<sub>2</sub> at room temperature significantly outperforms that of pristine ε-MnO<sub>2</sub> and commercially activated MnO<sub>2</sub> (C-MnO<sub>2</sub>). We further elucidate how O<sub>v</sub> promote O<sub>2</sub> chemisorption and spontaneous activation through structural characterizations and density functional theory (DFT) calculations. Moreover, the pivotal roles of ROS in the oxidation process through controlled quenching experiments are also verified. This work offers a practical strategy and theoretical insights for constructing environmentally friendly Mn-based catalysts and producing highly desirable <sup>1</sup>O<sub>2</sub> for efficient aerobic oxidation.

## Results and discussion

### Synthesis and characterization

Compartmentalized microemulsions, stabilized by an excess of surfactants, serve as versatile miniature reactors for the synthesis of N<sub>y</sub>-MnO<sub>2</sub> to spontaneously produce <sup>1</sup>O<sub>2</sub> (Scheme 1). Within the confined aqueous microdroplets, isonitrile acid produced by urea decomposition reacts with Mn<sup>2+</sup> to form catalyst precursor, manganese carbonate (MnCO<sub>3</sub>), as verified by X-ray diffraction (XRD) patterns in Fig. S1a.† Fourier transform infrared (FTIR) spectra in Fig. S1b† display the presence of new peaks at 1443 cm<sup>-1</sup>, 866 cm<sup>-1</sup>, and 720 cm<sup>-1</sup>, further confirming the successful formation of MnCO<sub>3</sub>.<sup>33,34</sup> Following calcination in air, MnCO<sub>3</sub> decomposes into MnO<sub>2</sub>. The XRD patterns of the N<sub>y</sub>-MnO<sub>2</sub> nanocatalysts, as shown in Fig. 1a, are identified as ε-MnO<sub>2</sub>. The disappearance of the broad band at 1443 cm<sup>-1</sup> and the emergence of peak at 1385 cm<sup>-1</sup> in FTIR spectra indicates the incorporation of N atoms into ε-MnO<sub>2</sub> (Fig. S1b†). Additionally, X-ray photoelectron spectroscopy (XPS) was employed to analyze the embedded N in N<sub>55</sub>-MnO<sub>2</sub>. The distinct peak at 399.6 eV in the N 1s spectra of N<sub>y</sub>-MnO<sub>2</sub> (Fig. 1b and S2†) is unequivocally attributed to N atoms inserted



Scheme 1 Schematic illustration of the preparation of N<sub>y</sub>-MnO<sub>2</sub> nanocatalysts using compartmentalized microdroplets.



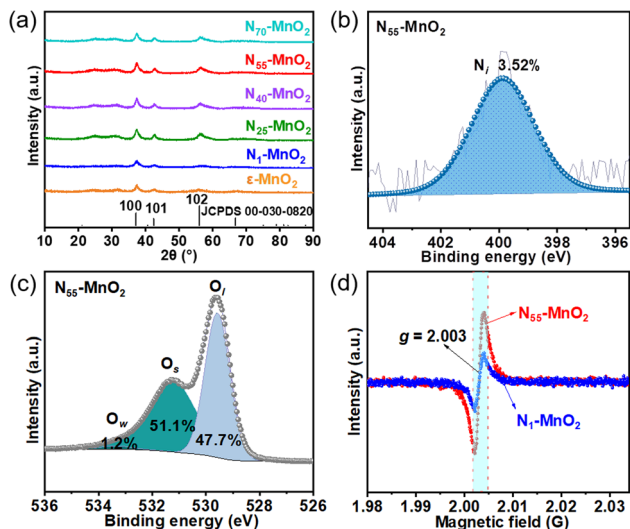


Fig. 1 (a) XRD patterns of  $N_y$ -MnO<sub>2</sub> ( $y = 1, 25, 40, 55, 70$ ) and  $\epsilon$ -MnO<sub>2</sub>; (b) N 1s and (c) O 1s XPS spectra of  $N_{55}$ -MnO<sub>2</sub> ( $O_w$ : oxygen from water adsorption); (d) EPR spectra of  $N_1$ -MnO<sub>2</sub> and  $N_{55}$ -MnO<sub>2</sub>.

at interstitial sites.<sup>35</sup> The introduction of interstitial N minimizes the formation energy of  $O_v$  and facilitates the generation of high-concentration  $O_v$ .<sup>35</sup> As a result, the  $N_{55}$ -MnO<sub>2</sub> catalyst, with an optimal interstitial N content, achieves a maximum concentration of surface oxygen atoms ( $O_s$ ) at 51.1% in the vicinity of  $O_v$  (Fig. 1c, S3, and Table S1†).<sup>36,37</sup> In addition, the  $O_s$  content and the unsaturated Mn coordination ( $Mn^{3+}/Mn^{4+}$  ratio of 0.90, as shown in Fig. S4†), in  $N_{55}$ -MnO<sub>2</sub>, significantly exceed that of similar catalysts (Table S2†).<sup>37–41</sup> Furthermore, the evolutionary trend facilitated by interstitial N-doping is reflected in the increased-intensity peak of  $O_v$  at  $g = 2.003$  in the electron paramagnetic resonance (EPR) spectrum in Fig. 1d. However, excessive N-doping in  $N_{70}$ -MnO<sub>2</sub> tends to occupy the formed vacancies, negatively affecting  $O_v$  formation (Fig. S3e†). As observed by transmission electron microscopy (TEM) in Fig. 2a, the  $N_{55}$ -MnO<sub>2</sub> catalyst possesses a size of  $\sim 115$  nm, which is consistent with the results from dynamic light scattering (DLS,

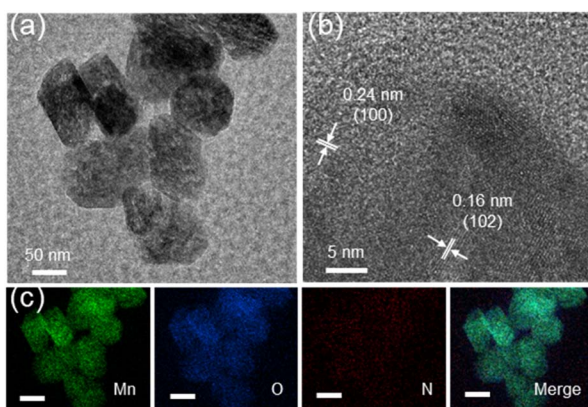


Fig. 2 (a)TEM, (b) HRTEM, and (c) EDS elemental mapping images (scale bars, 50 nm) of  $N_{55}$ -MnO<sub>2</sub> nanocatalyst.

Fig. S1c†). This demonstrates the distinctive compartmentalization effect of microemulsions in synthesizing uniform-size nanocatalysts. Additionally, High-resolution TEM (HRTEM) image of  $N_{55}$ -MnO<sub>2</sub> reveals  $d$ -spacings of 0.24 nm and 0.16 nm (Fig. 2b), corresponding to the (100) and (102) facets, respectively, of  $\epsilon$ -MnO<sub>2</sub>.<sup>42</sup> Energy dispersive spectroscopy (EDS) element mapping images of  $N_{55}$ -MnO<sub>2</sub> demonstrate that interstitial N is uniformly embedded in the MnO<sub>2</sub> lattice (Fig. 2c). Doping interstitial N into MnO<sub>2</sub> leads to alterations in the original electronic structure and unsaturated coordination environment, thus enhancing the catalytic oxidation capacity.<sup>37</sup> This is confirmed through hydrogen temperature-programmed reduction ( $H_2$ -TPR), with  $N_{55}$ -MnO<sub>2</sub> displaying the most prominent redox capability (Fig. S1d†), consistent with previous reports.<sup>37,43–47</sup> Additionally, Brunauer-Emmett-Teller (BET) analysis of  $N_2$  adsorption-desorption measurements was conducted to assess the BET parameters of  $N_y$ -MnO<sub>2</sub>. As shown in Fig. S5 and Table S3,†  $N_{55}$ -MnO<sub>2</sub> exhibits the highest BET surface area of  $78.7$  m<sup>2</sup> g<sup>-1</sup> among the  $N_y$ -MnO<sub>2</sub> samples and an average mesopore size of 11.41 nm. This can be attributed to the presence of  $O_v$  in  $N_y$ -MnO<sub>2</sub>, which contribute to the formation of abundant mesopores on the surface of  $N_y$ -MnO<sub>2</sub>.<sup>48</sup>

### Adsorption of O<sub>2</sub> and production of <sup>1</sup>O<sub>2</sub>

Previous studies have demonstrated that an increased concentration of  $O_v$  enhances the chemical adsorption of O<sub>2</sub>, leading to the elongation of the O–O bond and facilitating O<sub>2</sub> activation.<sup>24,25,48</sup> Our DFT calculations reveal that the adsorption energy of O<sub>2</sub> on the surface of  $\epsilon$ -MnO<sub>2</sub> is  $-1.24$  eV, whereas it decreases to  $-2.18$  eV on  $N_{55}$ -MnO<sub>2</sub> (Fig. 3a). This indicates that the augmented  $O_v$  resulting from N-doping reduces the adsorption energy of O<sub>2</sub>, thereby promoting its chemisorption and excitation.<sup>25</sup> To gain further insights, we employed *in situ* IR spectroscopy for real-time monitoring of O<sub>2</sub> adsorption and activation on the surface of  $N_{55}$ -MnO<sub>2</sub>. As shown in Fig. 3b, a chemisorption peak of O<sub>2</sub> emerges at  $1401$  cm<sup>-1</sup> in an O<sub>2</sub> atmosphere, followed by the gradual formation of a robust band corresponding to surface-bonded superoxide anion species ( $O_2^{\cdot-}$ ) at  $1052$  cm<sup>-1</sup>.<sup>49,50</sup> This illustrates the role of  $O_v$  in promoting O<sub>2</sub> activation. Conversely, no discernible peaks are observed under an O<sub>2</sub> + H<sub>2</sub>O vapor atmosphere, possibly due to H<sub>2</sub>O occupying the  $O_v$  and preventing O<sub>2</sub> adsorption (Fig. S6a†).

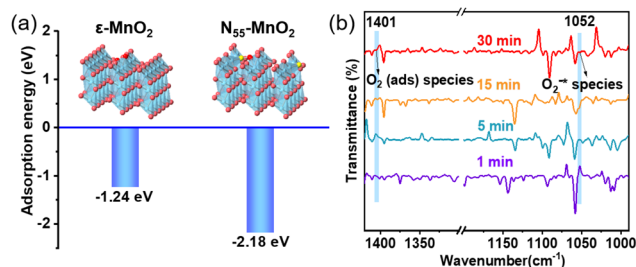


Fig. 3 (a) Adsorption energy of O<sub>2</sub> on the surface of pristine  $\epsilon$ -MnO<sub>2</sub> and  $N_{55}$ -MnO<sub>2</sub> obtained by DFT calculation; (b) *in situ* IR spectra of O<sub>2</sub> adsorbed onto the surface of  $N_{55}$ -MnO<sub>2</sub>.



The direct interactions between  $O_2$  and  $N_y$ - $MnO_2$  were investigated without light irradiation using EPR. 2,2,6,6-tetramethylpiperidine (TEMP) was employed as a quencher to capture  $^1O_2$  activated by  $N_y$ - $MnO_2$  at room temperature. As depicted in Fig. 4a and b,  $N_1$ - $MnO_2$ , which exhibits fewer  $O_v$ , generates only  $^{\bullet}O_2^-$  and not  $^1O_2$ . With an increase in urea feeding, enhanced N-doping promotes  $O_v$  formation in  $N_y$ - $MnO_2$ . Notably, distinct triple peaks corresponding to  $TEMP-^1O_2$  are evident for both  $N_{55}$ - $MnO_2$  and  $N_{25}$ - $MnO_2$ , with an intensity ratio of 1:1:1.<sup>25</sup> The intensity of the  $^1O_2$  peak strengthens with higher  $O_v$  content, underscoring the significant role of  $O_v$  in activating  $O_2$ . Quantitative EPR analysis indicates that  $N_{55}$ - $MnO_2$  generates  $^1O_2$  at an average rate of  $5.94 \text{ mol g}_{\text{cat}}^{-1} \text{ L}^{-1} \text{ min}^{-1}$  (Fig. 4c). Importantly,  $N_y$ - $MnO_2$  doesn't produce highly reactive hydroxyl radicals ( $^{\bullet}OH$ , Fig. S6†).<sup>51,52</sup> To investigate the contribution of  $O_v$  to the excitation of  $O_2$ , various  $\epsilon$ - $MnO_2$  nanocatalysts were synthesized and characterized without N doping (Fig. S7–S9†). Interestingly,  $\epsilon$ - $MnO_2$ -*n*-350 (where 350 indicates the thermal treatment temperature), with the highest  $O_s$  concentration of 44.4%, demonstrates the capability to generate  $^1O_2$  under mild conditions (Fig. S10†). These findings underscore the pivotal role played by abundant surface-exposed  $O_v$  in nano-sized  $MnO_2$  for the self-activation of  $O_2$ . However, the catalytic activity of  $\epsilon$ - $MnO_2$ -*n*-350 is still much lower than that of  $N_{55}$ - $MnO_2$  can be attributed to the doping effect of interstitial N, which will be further discussed later.

To investigate the roles of ROS in the reaction, controlled quenching experiments were conducted. As shown in Fig. 4d, the conversion of benzyl alcohol sharply decreases from >99.9% to 26% after the addition of TEMPO as a ROS quencher, indicating that ROS mediate the oxidative reaction. Upon separately introducing 1,4-benzoquinone (BQ) and isopropyl alcohol (IPA), the conversion of benzyl alcohol decreases slightly, illustrating that  $^{\bullet}O_2^-$  and  $^{\bullet}OH$  play subsidiary roles in the selective

oxidation process. Surprisingly, the oxidation reaction is nearly halted when furfuryl alcohol (FA) is used to capture  $^1O_2$ . This undeniable evidence confirms  $^1O_2$  as the primary ROS in this  $O_2$ -mediated oxidative reaction. In summary,  $^1O_2$  is spontaneously generated through the direct activation of  $O_2$ , rather than the oxidation of  $^{\bullet}O_2^-$  observed in photocatalytic processes.<sup>52</sup> Despite  $O_2$  being the source of ROS, the conversion of benzyl alcohol can be achieved at 31% and 25.5% under  $N_2$  and Ar atmospheres, respectively (Fig. 4d, S11, and Table S4†). This is attributed to the involvement of  $O_1$  in the aerobic oxidation process, following the MVK mechanism, which is consistent with previous reports.<sup>17,44</sup>

### Selective oxidation of alcohols

Aerobic oxidation of alcohols serves as a widely important model reaction for assessing the oxidative activity of the catalyst. However, effectively exciting  $O_2$  with catalysts remains a challenge.<sup>15,20</sup> If a catalyst can spontaneously generate  $^1O_2$  from the ground-state oxygen, it will significantly advance the development of environmentally friendly catalysis. The plausible reaction process for efficient oxidation by  $N_y$ - $MnO_2$  is presented in Fig. 5.  $O_v$  and interstitial N sites promote  $O_2$  adsorption on the surface of  $N_y$ - $MnO_2$ , while  $O_v$  elongate the O–O bonds, facilitating direct excitation of  $O_2$  to  $^1O_2$  for efficient alcohol oxidation. We evaluate the catalytic performance of  $N_y$ - $MnO_2$  for the aerobic oxidation of benzyl alcohol under  $O_2$  bubbling conditions. We observe that micrometer-scale  $\epsilon$ - $MnO_2$  displays low activity (conversion rate of 18.2% in 2.5 hours) due to its inability to activate  $O_2$  to form  $^1O_2$  (Fig. 6a and S10†). The C- $MnO_2$  exhibits negligible activity (Fig. S12 and S13†). In contrast,  $N_{55}$ - $MnO_2$  achieves 99.9% conversion and 99.9% selectivity in 2.5 hours, with a turnover frequency (TOF) 7.4 and 6.7 times higher than that of  $\epsilon$ - $MnO_2$  and  $\epsilon$ - $MnO_2$ -*n*-350, respectively (Fig. 6b and Table S5†).

To unravel the catalytic reaction mechanism, we conducted kinetics studies using various catalysts. It can be observed that the initial reaction rate remains constant under different  $O_2$  pressures, indicating independence from  $O_2$  pressure variations (Fig. S14 and Tables S6–S8†). Through calculation and fitting,

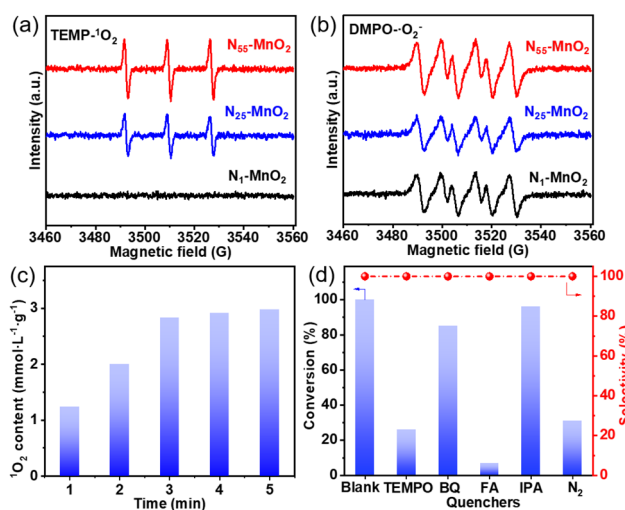


Fig. 4 The characteristic peaks of (a)  $TEMP-^1O_2$  and (b)  $DMPO-^{\bullet}O_2^-$  captured by EPR; (c) the content of  $^1O_2$  produced by  $N_{55}$ - $MnO_2$ ; (d) the controlling experiment catalyzed by  $N_{55}$ - $MnO_2$  with different quenchers.



Fig. 5 Plausible reaction process for efficient oxidation by  $N_y$ - $MnO_2$  activating  $O_2$  to form  $^1O_2$ .



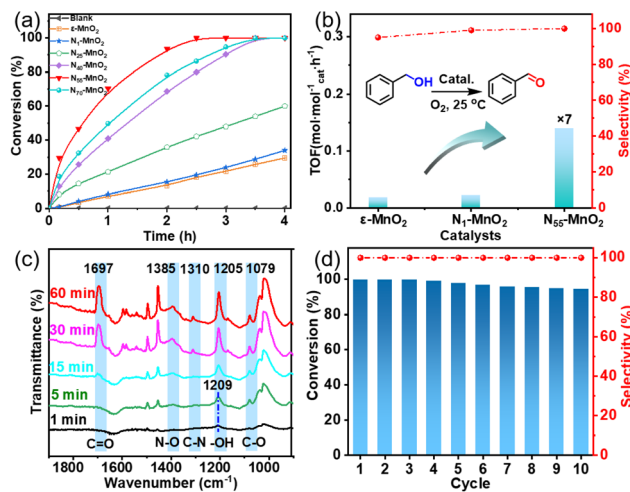


Fig. 6 (a) Aerobic oxidation of benzyl alcohol using activated  $\epsilon$ -MnO<sub>2</sub> and N<sub>y</sub>-MnO<sub>2</sub> ( $y = 1, 25, 40, 55, 70$ ), (b) the comparison of TOF of  $\epsilon$ -MnO<sub>2</sub>, N<sub>1</sub>-MnO<sub>2</sub>, and N<sub>55</sub>-MnO<sub>2</sub> (TOF = moles of benzyl alcohol converted per mole of catalyst/reaction time); (c) *in situ* IR spectra of oxidation of benzyl alcohol on the surface of N<sub>55</sub>-MnO<sub>2</sub>; (d) the recyclability of N<sub>55</sub>-MnO<sub>2</sub> for aerobic oxidation of benzyl alcohol.

the reaction is found to be correlated with the concentration of benzyl alcohol, further demonstrating a first-order reaction (Tables S9 and S10<sup>†</sup>). Furthermore, we calculate the activation energies ( $E_a$ ) of the N<sub>1</sub>-MnO<sub>2</sub>, N<sub>25</sub>-MnO<sub>2</sub>, and N<sub>55</sub>-MnO<sub>2</sub> catalysts using the Arrhenius equation, resulting in values of 55.04 kJ mol<sup>-1</sup>, 45.87 kJ mol<sup>-1</sup>, and 43.17 kJ mol<sup>-1</sup>, respectively (Fig. S15 and Tables S11–S13<sup>†</sup>). Evidently, the catalytic performance of N<sub>y</sub>-MnO<sub>2</sub> is positively correlated with its O<sub>v</sub> content, providing further evidence of the role of O<sub>v</sub> in the oxidation process. *In situ* IR spectra were utilized to analyze the dynamic process of benzyl alcohol oxidation on the surface of N<sub>55</sub>-MnO<sub>2</sub>, revealing enhanced catalytic performance. Under an O<sub>2</sub> atmosphere, N<sub>55</sub>-MnO<sub>2</sub> serves as the background for data acquisition. In the first five minutes, four characteristic peaks emerge in Fig. 6c. Compared with C-MnO<sub>2</sub> (Fig. S16<sup>†</sup>), the newly appeared N–O peak at 1385 cm<sup>-1</sup> on N<sub>55</sub>-MnO<sub>2</sub> is attributed to O<sub>2</sub> adsorption by interstitial N sites. At 1310 cm<sup>-1</sup>, the band corresponds to the stretching vibration of C–N bonds. The formation of C–N bonds is facilitated by the chemisorption of –OH groups from alcohol onto the interstitial N sites. After exposure to an O<sub>2</sub> flow for 15 minutes, the O–H band shifts from 1209 cm<sup>-1</sup> to 1205 cm<sup>-1</sup>, indicating an interaction between the adsorbed O<sub>2</sub> species and –C–OH groups on benzyl alcohol. Continuing the exposure for 30 minutes, the broad C=O band at 1697 cm<sup>-1</sup> signifies the formation of benzyl aldehyde catalyzed by N<sub>55</sub>-MnO<sub>2</sub>.

Semiconductor catalysts have recently demonstrated an enhanced capacity for generating <sup>1</sup>O<sub>2</sub> when exposed to light, resulting in improved oxidation performance.<sup>24,25</sup> In contrast, N<sub>55</sub>-MnO<sub>2</sub> exhibits virtually unchanged activity under both light and dark conditions (Table S4<sup>†</sup>). This observation suggests that the inherent capability of N<sub>55</sub>-MnO<sub>2</sub> to spontaneously generate <sup>1</sup>O<sub>2</sub> operates independently of external factors, marking

a significant difference from previously reported studies.<sup>25,50,53,54</sup>

Compared to recently reported heterogeneous catalysts, the well-designed N<sub>y</sub>-MnO<sub>2</sub> nanocatalysts display a unique ability to spontaneously generate sufficient <sup>1</sup>O<sub>2</sub> under mild reaction conditions. This enables the green and efficient conversion of alcohols without the need for light or additives, showcasing their superior catalytic activity (Table S14<sup>†</sup>).

Furthermore, we investigated the applicable substrate scope of aerobic oxidation. As shown in Table 1, aromatic primary alcohols, including benzyl alcohol and its derivatives, exhibit yields of over 99.9% for the corresponding aldehydes. Even for aromatic secondary alcohols, yields exceeding 99.9% are obtained when the reaction time extends to 6.0 hours. In comparison, the catalytic performance of N<sub>55</sub>-MnO<sub>2</sub> in the oxidation of aliphatic alcohols (*e.g.*, 1-hexanol) is hampered by significant

Table 1 Catalytic activity of N<sub>55</sub>-MnO<sub>2</sub> for aerobic oxidation of various alcohols<sup>a</sup>

Entry	Product	Conv. (%)	Sel. (%)	Yield (%)
1		99.9	>99.9	>99.9
2		99.9	>99.9	>99.9
3		99.9	>99.9	>99.9
4		82.6	>99.9	>82.6
5		99.9	>99.9	>99.9
6		99.9	>99.9	>99.9
7		99.9	>99.9	>99.9
8		99.9	>99.9	>99.9
9		99.9	>99.9	>99.9
10 <sup>b</sup>		99.9	>99.9	30.5
11 <sup>b</sup>		99.9	>99.9	47.3
12		n.d.	—	n.d.

<sup>a</sup> Reaction condition: 5.0 mL of toluene, 0.5 mmol of alcohols, 150.0 mg of N<sub>55</sub>-MnO<sub>2</sub>, 1200 rpm, 25.0 ± 1.0 °C, O<sub>2</sub> flow 16.0 mL min<sup>-1</sup> 1.0 bar, reaction time 2.5 h, n. d. not detect. <sup>b</sup> Reaction time 6.0 h.



steric hindrance effects. Using benzyl alcohol as the model substrate, we evaluate the recyclability of  $N_{55}\text{-MnO}_2$  in aerobic oxidation. As depicted in Fig. 6d,  $N_{55}\text{-MnO}_2$  maintains >94% conversion of benzyl alcohol and >99.9% selectivity toward aldehydes over ten cycles. Additionally, XRD and XPS characterizations confirm the stability of the recycled  $N_{55}\text{-MnO}_2$  structure (Fig. S17†). To the best of our knowledge, results demonstrating both sufficient formation of  $^1\text{O}_2$  and the green oxidation of alcohols under mild conditions have been scarcely reported.

## Conclusions

In conclusion, we have successfully developed a range of  $N_y\text{-MnO}_2$  nanocatalysts capable of directly generating  $^1\text{O}_2$  at room temperature for the aerobic oxidation of alcohols. The *in situ* insertion of interstitial N into  $\text{MnO}_2$  within encapsulated aqueous microreactors can lead to  $\text{O}_s$  concentrations of up to 51.1% for  $N_{55}\text{-MnO}_2$  and enhance chemisorption of reactants. Consequently, these well-synthesized  $N_y\text{-MnO}_2$  nanocatalysts have demonstrated enhanced redox performance due to their higher surface  $\text{O}_v$  exposure and N-doping. DFT calculations have revealed that the interstitial N and increased  $\text{O}_v$  content facilitates the chemisorption of  $\text{O}_2$ , resulting in the generation of sufficient  $^1\text{O}_2$ . Under aerobic oxidation conditions, the  $N_{55}\text{-MnO}_2$  catalyst has achieved alcohol conversion rates exceeding 99.9% and aldehyde selectivity of over 99.9%, without the use of additives. Additionally, the  $N_{55}\text{-MnO}_2$  catalyst has displayed a TOF value of  $0.14 \text{ mol mol}_{\text{cat}}^{-1} \text{ h}^{-1}$ , 6.7 times higher than that of the N-undoped  $\epsilon\text{-MnO}_2$  catalyst. Furthermore,  $N_{55}\text{-MnO}_2$  has shown excellent catalytic stability after ten cycles, remaining robust even after recycling and calcination under an air atmosphere. This study introduces a strategy for fabricating efficient ROS triggers within compartmentalized microdroplets, resulting in the generation of favorable  $^1\text{O}_2$  to facilitate the aerobic oxidation of alcohols.

## Experimental

### Synthesis of $N_y\text{-MnO}_2$ catalyst

A homogeneous oil phase was achieved through vigorous mechanical stirring of sodium dodecyl benzene sulfonate (10.5 g) and xylene (90 mL). Subsequently, a mixture containing manganese(II) nitrate tetrahydrate (10 mmol), water (5.4 mL), and urea (1, 25, 40, 55, 70 mmol) was gently introduced into the aforementioned oil phase, resulting in the formation of a water-in-oil (W/O) microemulsion. After stirring for 30 min, the resulting microemulsion was transferred to a 100 mL Teflon autoclave and hydrothermally treated at 160 °C for 8 h. Finally, the received gray precursor was dried overnight under vacuum, and heated at 350 °C in a muffle furnace to obtain  $N_y\text{-MnO}_2$  catalyst, where  $y$  represents the molar amount of urea used.

### Catalytic performance of aerobic oxidation

$N_y\text{-MnO}_2$  (150 mg), toluene (5 mL), and benzyl alcohol (0.5 mmol) were charged into a Schleck flask, and the temperature

was maintained at  $25.0 \pm 1.0$  °C. The reaction mixture was stirred magnetically at 1200 rpm, while  $\text{O}_2$  was continuously bubbled at a rate of  $16 \text{ mL min}^{-1}$ . After several hours of reaction, the mixture was analyzed by gas chromatography (PANNA A91Plus). The used  $N_y\text{-MnO}_2$  was recycled by high-speed centrifugation and subsequently calcined at 350 °C for 4 h.

### ROS trapping experiment

The ROS control experiments followed procedures similar to the aerobic oxidation process. In these experiments, benzyl alcohol and FA were employed as the model substrate and  $^1\text{O}_2$  scavenger, respectively.  $N_y\text{-MnO}_2$  (150.0 mg), toluene (5.0 mL), benzyl alcohol (0.5 mmol), and FA (1.0 mmol) were sequentially introduced into a reaction tube, maintaining the temperature at  $25.0 \pm 1.0$  °C. The mixture underwent magnetic stirring (1200 rpm) with a continuous  $\text{O}_2$  flow ( $16.0 \text{ mL min}^{-1}$ ). Upon completion of the reaction, the conversion of benzyl alcohol was assessed using gas chromatography. Additionally, experiments involving TEMPO, BQ and IPA quenchers were conducted following the aforementioned procedures. The roles of ROS ( $^1\text{O}_2$ ,  $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$ ) in oxidative reaction were analyzed based on the observed oxidation of benzyl alcohol.

## Author contributions

J. T. and J. C.: conceptualization, methodology, writing – original draft. Y. Z. Q. M. and P. C.: chemical experiments and analysed the data. Y. K., L. F., J. K., and T. H. participated in various aspects of the experiments and discussions. X. H., P. L. and Z. L.: recycling experiments. C. W., Q. K., Y. K., and Y. Y. review & editing, supervision.

## Conflicts of interest

There are no conflicts to declare.

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## References

- C. Lu, C. Zhang, P. Wang, Y. Zhao, Y. Yang, Y. Wang, H. Yuan, S. Qu, X. Zhang, G. Song and K. Pu, *Chem*, 2020, **6**, 2314–2334.
- C. Bloyet, F. Sciortino, Y. Matsushita, P. A. Karr, A. Liyanage, W. Jevasuwan, N. Fukata, S. Maji, J. Hynek, F. D'Souza, L. K. Shrestha, K. Ariga, T. Yamazaki, N. Shirahata, J. P. Hill and D. T. Payne, *J. Am. Chem. Soc.*, 2022, **144**, 10830–10843.
- X. Bao, H. Li, Z. Wang, F. Tong, M. Liu, Z. Zheng, P. Wang, H. Cheng, Y. Liu, Y. Dai, Y. Fan, Z. Li and B. Huang, *Appl. Catal., B*, 2021, **286**, 119885.
- X. Liu, H. Yu, J. Huang, J. Su, C. Xue, X. Zhou, Y. He, Q. He, D. Xu, C. Xiong and H. Ji, *Chem. Sci.*, 2022, **13**, 9560–9568.
- D. Kalaitzakis, A. Bosveli, K. Sfakianaki, T. Montagnon and G. Vassilikogiannakis, *Angew. Chem., Int. Ed.*, 2021, **133**, 4381–4387.
- W. Wu, C. Han, Q. Zhang, Q. Zhang, Z. Li, D. J. Gosztola, G. P. Wiederrecht and M. Wu, *J. Catal.*, 2018, **361**, 222–229.
- Q. Ke, S. Fang, J. Tang, F. Li, C. Ning, Z. Tang, Q. Ling, X. Liu and P. Cui, *ChemPhotoChem*, 2022, **6**, e202200075.
- L. Kong, G. Fang, X. Xi, Y. Wen, Y. Chen, M. Xie, F. Zhu, D. Zhou and J. Zhan, *Chem. Eng. J.*, 2021, **403**, 126445.
- H. Ma, S. Long, J. Cao, F. Xu, P. Zhou, G. Zeng, X. Zhou, C. Shi, W. Sun, J. Du, K. Han, J. Fan and X. Peng, *Chem. Sci.*, 2021, **12**, 13809–13816.
- C. Lin, S. M. Bachilo and R. B. Weisman, *J. Am. Chem. Soc.*, 2020, **142**, 21189–21196.
- R. Gao, X. Mei, D. Yan, R. Liang and M. Wei, *Nat. Commun.*, 2018, **9**, 2798.
- N. Singh, P. Kumar, R. Kumar and U. Riaz, *Ind. Eng. Chem. Res.*, 2019, **58**, 14044–14057.
- Y. Chen, Z. Wang, H. Wang, J. Lu, S. Yu and H. Jiang, *J. Am. Chem. Soc.*, 2017, **139**, 2035–2044.
- R. Long, K. Mao, X. Ye, W. Yan, Y. Huang, J. Wang, Y. Fu, X. Wang, X. Wu, Y. Xie and Y. Xiong, *J. Am. Chem. Soc.*, 2013, **135**, 3200–3207.
- J. Huang, S. He, J. L. Goodsell, J. R. Mulcahy, W. Guo, A. Angerhofer and W. D. Wei, *J. Am. Chem. Soc.*, 2020, **142**, 6456–6460.
- W. Zhang, W. Huang, J. Jin, Y. Gan and S. Zhang, *Appl. Catal., B*, 2021, **292**, 120197.
- J. Tang, Y. Cao, F. Ruan, F. Li, Y. Jin, M. N. Ha, X. Han and Q. Ke, *Ind. Eng. Chem. Res.*, 2020, **59**, 9408–9413.
- J. Chen, H. Tang, M. Huang, Y. Yan, J. Zhang, H. Liu, J. Zhang, G. Wang and R. Wang, *ACS Appl. Mater. Interfaces*, 2021, **13**, 26960–26970.
- F. Ruan, F. Li, Z. Dong, Q. Ke, Y. Jin, W. Zhan, M. N. Ha and J. Tang, *Green Synth. Catal.*, 2021, **2**, 38–44.
- M. Koutani, E. Hayashi, K. Kamata and M. Hara, *J. Am. Chem. Soc.*, 2022, **144**, 14090–14100.
- Q. Ke, Y. Jin, F. Ruan, M. N. Ha, D. Li, P. Cui, Y. Cao, H. Wang, T. Wang, V. N. Nguyen, X. Han, X. Wang and P. Cui, *Green Chem.*, 2019, **21**, 4313–4318.
- Y. Pérez-Badell, X. Solans-Monfort, M. Sodupe and L. A. Montero, *Phys. Chem. Chem. Phys.*, 2010, **12**, 442–452.
- J. Oviedo and M. J. Gillan, *Surf. Sci.*, 2001, **490**, 221–236.
- Y. Hao, B. Liu, L. Tian, F. Li, J. Ren, S. Liu, Y. Liu, J. Zhao and X. Wang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 12687–12693.
- J. Wang, X. Xu, Y. Liu, Z. Wang, P. Wang, Z. Zheng, H. Cheng, Y. Dai and B. Huang, *ChemSusChem*, 2020, **13**, 3488–3494.
- S. Tan, Y. Ji, Y. Zhao, A. Zhao, B. Wang, J. Yang and J. G. Hou, *J. Am. Chem. Soc.*, 2011, **133**, 2002–2009.
- M. Setvín, U. Aschauer, P. Scheiber, Y. Li, W. Hou, M. Schmid, A. Selloni and U. Diebold, *Science*, 2013, **341**, 988–991.
- M. Li, S. You, X. Duan and Y. Liu, *Appl. Catal., B*, 2022, **312**, 121419.
- X. Kang, G. Dong and T. Dong, *ACS Appl. Energy Mater.*, 2023, **6**, 1025–1036.
- Y. Zhuo, X. Guo, W. Cai, T. Shao, D. Xia, C. Li and S. Liu, *Appl. Catal., B*, 2023, **333**, 122789.
- M. Yang, K. Wu, S. Sun, J. Duan, X. Liu, J. Cui, S. Liang and Y. Ren, *ACS Catal.*, 2023, **13**, 681–691.
- J. Tang, Q. Zhang, K. Hu, P. Zhang and J. Wang, *J. Catal.*, 2017, **353**, 192–198.
- M. Liu, Q. Wang, Z. Liu, Y. Zhao, X. Lai, J. Bi and D. Gao, *Chem. Eng. J.*, 2020, **383**, 123161.
- P. V. Vardhan, M. B. Idris, H. Y. Liu, S. R. Sivakkumar, P. Balaya and S. Devaraj, *J. Electrochem. Soc.*, 2018, **165**, A1865.
- T. He, X. Zeng and S. Rong, *J. Mater. Chem. A*, 2020, **8**, 8383–8396.
- T. J. Frankcombe and Y. Liu, *Chem. Mater.*, 2023, **35**, 5468–5474.
- G. Qi, X. Liu, C. Li, C. Wang and Z. Yuan, *Angew. Chem., Int. Ed.*, 2019, **58**, 17406–17411.
- L. Liu, R. Liu, T. Xu, Q. Zhang, Y. Tan, Q. Zhang, J. Ding and Y. Tang, *Inorg. Chem.*, 2020, **59**, 14407–14414.
- S. Rong, K. Li, P. Zhang, F. Liu and J. Zhang, *Catal. Sci. Technol.*, 2018, **8**, 1799–1812.
- Y. Huang, Y. Liu, W. Wang, M. Chen, H. Li, S. Lee, W. Ho, T. Huang and J. Cao, *Appl. Catal., B*, 2020, **278**, 119294.
- F. Morales, D. Grandjean, A. Mens, F. M. F. Groot and B. M. Weckhuysen, *J. Phys. Chem. B*, 2006, **110**, 8626–8639.
- Y. Xu, J. Dhainaut, G. Rochard, J. Dacquain, A. Mamede, J. Giraudon, J. Lamonier, H. Zhang and S. Royer, *Chem. Eng. J.*, 2020, **388**, 124146.
- J. Tang, B. Jiao, W. Chen, F. Ruan, F. Li, P. Cui, C. Wan, M. N. Ha, V. N. Nguyen and Q. Ke, *Nano Res.*, 2022, **15**, 6076–6083.
- Y. Jin, F. Li, P. Cui, Y. Yang, Q. Ke, M. N. Ha, W. Zhan, F. Ruan, C. Wan, Z. Lei, V. N. Nguyen, W. Chen and J. Tang, *Nano Res.*, 2021, **14**, 2637–2643.
- Q. Ke, D. Yi, Y. Jin, F. Lu, B. Zhou, F. Zhan, Y. Yang, D. Gao, P. Yan, C. Wan, P. Cui, D. Golberg, J. Yao and X. Wang, *ACS Sustain. Chem. Eng.*, 2020, **8**, 5734–5741.



- 46 H. Li, Y. Zhang, J. Tang, G. Huang, P. Cui and Q. Ke, *Green Synth. Catal.*, 2022, DOI: [10.1016/j.gresc.2022.09.005](https://doi.org/10.1016/j.gresc.2022.09.005).
- 47 J. Yu, T. Zeng, H. Wang, H. Zhang, Y. Sun, L. Chen, S. Song, L. Li and H. Shi, *Chem. Eng. J.*, 2020, **394**, 124458.
- 48 H. Li, J. Shang, Z. Ai and L. Zhang, *J. Am. Chem. Soc.*, 2015, **137**, 6393–6399.
- 49 Y. Lin, Z. Liu, L. Yu, G. Zhang, H. Tan, K. Wu, F. Song, A. K. Mechler, P. P. M. Schleker, Q. Lu, B. Zhang and S. Heumann, *Angew. Chem., Int. Ed.*, 2021, **60**, 3299–3306.
- 50 F. Li, J. Tang, Q. Ke, Y. Guo, M. N. Ha, C. Wan, Z. Lei, J. Gu, Q. Ling, V. N. Nguyen and W. Zhan, *ACS Catal.*, 2021, **11**, 11855–11866.
- 51 J. Li, X. Wang, J. Tian, X. Zhang and F. Shi, *Rare Met.*, 2023, **42**, 1877–1887.
- 52 B. He, H. Jin, Y. Wang, C. Fan, Y. Wang, X. Zhang, J. Liu, R. Li and J. Liu, *Rare Met.*, 2022, **41**, 132–143.
- 53 N. Siemer, A. Lüken, M. Zalibera, J. Frenzel, D. Muñoz-Santiburcio, A. Savitsky, W. Lubitz, M. Muhler, D. Marx and J. Strunk, *J. Am. Chem. Soc.*, 2018, **140**, 18082–18092.
- 54 T. Xia, W. Gong, Y. Chen, M. Duan, J. Ma, X. Cui, Y. Dai, C. Gao and Y. Xiong, *Angew. Chem., Int. Ed.*, 2022, **61**, e202204225.

