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# Effect of surface morphology on catalytic activity for NO oxidation of $SmMn_2O_5$ nanocrystals

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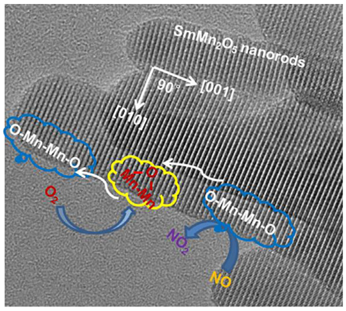
## HIGHLIGHTS

- $SmMn_2O_5$ nanocrystals are synthesized by a tunable hydrothermal route.
- The pH value of precursor solution is a decisive factor for morphology control.
- The nanoparticles exhibit better catalytic activity for NO oxidation than nanorods.
- The ability of surface oxygen adsorption is responsible for the performance improvement.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

$SmMn_2O_5$ has been reported to be a promising alternative to substitute the current commercial Pt-based catalysts for NO oxidation. In this work, single-crystalline orthorhombic $SmMn_2O_5$ nanorods and nanoparticles are successfully synthesized through a tunable hydrothermal route. The pH value of the precursor solution is a decisive factor for morphology control of $SmMn_2O_5$ nanocrystals, with decreasing pH value the morphology of $SmMn_2O_5$ nanocrystals converts from nanoparticles to nanorods. The nanoparticles exhibit a better catalytic activity for NO oxidation than the nanorods, because they can efficiently convert NO at lower temperature. By the analysis of X-ray photoelectron spectrum and high-resolution transmission electron microscope, the oxidation activity is found to be dependent on the high specific surface area and surface crystal planes of $SmMn_2O_5$ nanocrystals, which widens and deepens the oxygen chemistry and NO oxidation mechanism on the surfaces of $SmMn_2O_5$. This work could not only provide new insights into the morphology control of $SmMn_2O_5$ nanocrystals, but also pave a new way for the crystal planes modification of $SmMn_2O_5$ nanocrystals as NO oxidation catalyst to achieve an enhanced performance for environmental applications.

## 1. Introduction

In the exhaust gas of automotive engines are recognized as major nitrous oxides ($NO_x$) emissions sources, among which nitric oxide (NO) occupies the percent of ninety. Nitrous oxides ($NO_x$) is one of the main sources of air pollution, which can give rise to a lot of environmental problems, such as acid rain, photochemical and ozone depletion. Nitric oxide (NO) is a toxic gas, which can cause a lot of problems for human health, such as neurological diseases, emphysema and bronchitis. Hence, Nitrous oxides ($NO_x$) pollutants have attracted great attention due to its adverse effect on human and animal health and environment in general [1–3]. To date, one effective strategy is the use of selective

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catalytic for oxidizing portion NO to $NO_2$, subsequently, the selective catalytic reduction ($2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$) is adopted to remove $NO_x$ emissions. NO oxidation to $NO_2$ is a critical step to remove exhaust emission [4–6]. Therefore, the development of catalyst with high activity, selectivity and stability is particularly important to lean exhaust in diesel engines.

At present, platinum group metal catalysts dispersed on an oxide support have been widely used for the oxidation of NO in diesel engines due to their satisfactory performance. However, the high cost and poor stability restrain its application [7,8]. Over several decades, perovskite phase transition metal oxides have stimulated interest for high temperature applications in diesel exhaust. But the low surface area and complex composition lead it difficult to manufacture [9–11]. Recently, $SmMn_2O_5$ has been declared to be a promising and efficient high temperature to substitute the current commercial Pt-based catalysts for NO oxidation. Wang et al. showed that $SmMn_2O_5$ was synthesized through a coprecipitation method, which displayed superior catalytic activity for NO oxidation [12]. Zheng et al. verified that the superior catalytic performance of $SmMn_2O_5$ over $SmMnO_3$ for NO oxidation [13]. Feng et al. reported the $La_xSm_{1-x}Mn_2O_8$ (x = 0, 0.1, 0.3, 0.5) catalysts activity were enhanced by La substitution [14]. Therefore, $SmMn_2O_5$ is a high-promising NO oxidation catalysts, which is worth our further exploration.

The size and morphology of nanomaterials play crucial roles in its physical and chemical properties [15,16]. Previous studies on $YMn_2O_5$ nanocrystals have shown that their magnetic properties depend sensitively on the size of the material [17]. The elongated shape of $SmMn_2O_5$ nanoparticles were obtained by coprecipitation [18]. The $SmMn_2O_5$ nanorods were successfully synthesized by hydrothermal method [19]. However, to the best of our knowledge, the effect of size and morphology of $SmMn_2O_5$ on NO oxidation performance remains unclear. In especial, for the nanoscale $SmMn_2O_5$, with the decreasing of the size the activity of the surface is enhanced due to an increase in the surface of the unsaturated bond. It is becoming the focus of attention how to control the size of $SmMn_2O_5$ and analyze the internal process of NO conversion efficiency for the $SmMn_2O_5$ with different morphologies, which is conducive to further improve NO conversion efficiency and deeply understand the reaction mechanism. In this paper, $SmMn_2O_5$ nanorods and nanoparticles can be successfully synthesized via a simple hydrothermal process and the effect of hydrothermal parameters on the size and morphology of the $SmMn_2O_5$ nanocrystals are investigated. Besides, this work concentrates on the characterization of different morphology of $SmMn_2O_5$ nanocrystals and discusses the effect of surface morphology on catalytic activity for NO oxidation of $SmMn_2O_5$ nanocrystals. The correlative results would offer an efficient approach toward the morphology control of the $SmMn_2O_5$ nanocrystals, and put forward some new ideas about the performance improvement of NO oxidation catalyst.

## 2. Experimental section

### 2.1. Preparation of $SmMn_2O_5$

The raw materials included $Sm(NO_3)_3 \cdot 6H_2O$, $KMnO_4$ and $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ All chemicals were analytical grade and implemented without further purification. Preparation of $SmMn_2O_5$ nanocrystals was as follows. Firstly, 0.5 mmol $Sm(NO_3)_3 \cdot 6H_2O$, 0.3 mmol $KMnO_4$ and 0.7 mmol $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ were dissolved in a 50 mL beaker with 20 mL of distilled water under vigorous magnetic stirring. The molar ratio of $Sm:MnO_4^-:Mn^{2+}$ was 5:3:7, according to the chemical equation $5Sm^{3+} + 3MnO_4^- + 7Mn^{2+} + 26OH^- \rightarrow 5SmMn_2O_5 + 13H_2O$. Secondly, 0.3 M NaOH solution was slowly added into the homogenous solution and constantly stirred for several minutes to adjust the pH value of precursor solution, Finally, the mixtures were transferred into a 50 mL stainless steel Teflon-lined autoclave in an oven at a temperature of 200 °C for some time. After the hydrothermal reaction was expected to be completed, the system was cooled down to room temperature naturally. The obtained samples were centrifuged and washed with distilled water and alcohol three times. The final powder was dried at 60 °C for 12 h.

### 2.2. Characterization of $SmMn_2O_5$

The X-ray diffraction (XRD) was implemented by D/MAX-2500 instrument (Riguka, Japan) with Cu Kα radiation ($\lambda = 1.5406$ Å). In order to obtain the information of adsorption oxygen on the surface, the conventional X-ray photoelectron spectrum (XPS) was measured in Thermo ESCALAB 250 instrument using Al Kα as the excitation X-ray source. The morphology of samples was characterized with transmission electron microscope (JEM-2100, JEOL). In order to obtain Brunauer-Emmett-Teller (BET) surface area, the samples were analyzed by nitrogen adsorption at 77 K using a Micromeritics instrument (TriStar II 3020).

### 2.3. Characterization of NO conversion performance

The catalytic behavior of samples was carried at Altamira Instruments (AMI-300, America). 100 mg of the sample was placed in the middle of U-type quartz tubular with 5 mm internal diameters, which used a k-type thermocouple to measure the temperature. The adsorption of NO on the catalyst sample was carried out at room temperature with a flow of 450 ppm NO and 20% $O_2$ in $N_2$. The catalyst was heated up from 50 to 400 °C at a rate of 10 °C $min^{-1}$, which was kept for 30 min at each temperature to achieve a steady state. The $X_{NO}$(%) was defined as the percentage of NO conversation and it was calculated according to an equation:

$$X_{NO}(\%) = \{C_{NO,in} \rightarrow C_{NO,out}\}/C_{NO,in}$$

where $C_{NO,in}$ is the volumetric concentration of NO in the inlet gas and $C_{NO,out}$ is the volumetric concentration of NO in the outlet gas. The $T_{0.5}$ was defined as the corresponding temperature of 50% NO conversion ratio. Meanwhile, in order to compare with the NO conversation performance of the commercial $Pt/Al_2O_3$ catalysts, 2 wt% $Pt/Al_2O_3$ was measured under the same conditions.

## 3. Results and discussion

The influence of the precursor solution pH value is studied on the morphology and phase structure of $SmMn_2O_5$ and a set of experiments are carried out with different pH values from 3 to 12. Fig. 1 presents the XRD patterns of nanocrystals with different pH values from 3 to 9. It can

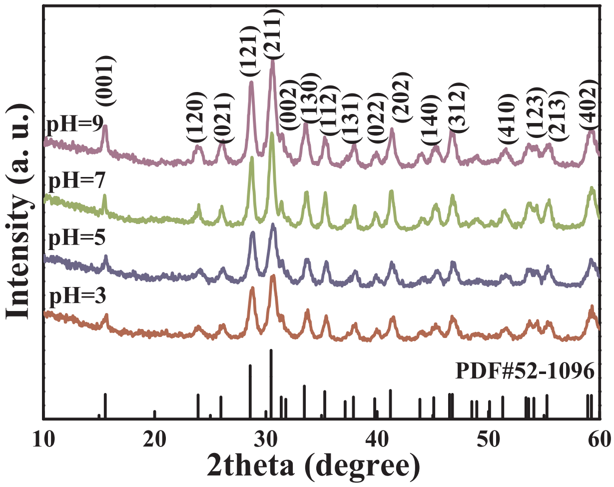

**Fig. 1.** XRD patterns of $SmMn_2O_5$ nanocrystals synthesized under different pH values at 200 °C for 12 h.