



Oriented growth of layered-MnO₂ nanosheets over α-MnO₂ nanotubes for enhanced room-temperature HCHO oxidation

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ABSTRACT

Construction of heterostructures with well-defined size, dimension, surface and interface is an effective approach to develop enhanced and unprecedented functionality. Herein, oriented growth of layered-MnO₂ nanosheets (L-MnO₂) over α-MnO₂ nanotubes backbones is demonstrated. The epitaxial relationship in the resulting α-MnO₂@L-MnO₂ heteroepitaxy is rationalized as (110)(α-MnO₂)||{(001)}(layered-MnO₂). With loading of 1 wt% Pt nanoparticles over the MnO₂ samples, the resulting Pt/MnO₂ samples show catalytic activity toward room-temperature HCHO oxidation via “HCHO + O₂ = CO₂ + H₂O”. Upon 1 h treatment, 92.1% HCHO becomes mineralized over the Pt/α-MnO₂@L-MnO₂, higher than that of 81.3% and 75.9% for the Pt/α-MnO₂ and Pt/L-MnO₂. The oxidation of HCHO was well fitted with the second-order kinetic model, with the rate constant of the Pt/α-MnO₂@L-MnO₂ exceeding that of the Pt/α-MnO₂ and the Pt/L-MnO₂ by 2.27 and 5.92 times. Density-Functional-Theory (DFT) simulations show that α-MnO₂ {100} surface facilitates adsorption/activation of O₂, and layered-MnO₂ {001} surface is beneficial to desorption of resultant H₂O. The α-MnO₂@L-MnO₂ heteroepitaxy simultaneously integrates exposed facets of α-MnO₂ {100} surface and layered-MnO₂ {001} surface, in which the synergistic effect of the two surfaces leads to significantly enhanced room-temperature HCHO oxidation activity. The present study provides a rational design of manganese oxide-based catalysts for advanced environmental and energy applications.

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1. Introduction

Indoor air quality is of prime importance since we spend three quarters time indoor. Volatile organic compounds (VOCs) are typical indoor air pollutants, which are mainly from building/decorative materials and unregulated indoor smoking. Formaldehyde (HCHO) is one of the most common VOC pollutants, causing profound impacts on human health. Therefore, strict environmental regulations are imposed to control indoor-air concentrations of gaseous HCHO [1]. In response, an assortment of technologies such as adsorption [2–4], plasma treatment [5,6], biological degradation [7], thermal catalytic oxidation [8–28] and photo-catalytic oxidation [29–31] are developed [1]. Amongst the aforementioned strategies, **room-temperature catalytic oxidation** is regarded as an affordable, convenient and complete disposal of

HCHO. The overall reaction of this method is represented as Reaction (1).



The key-enabling factor of room-temperature HCHO oxidation is to develop high-efficiency catalysts to sustain Reaction (1). Besides fast and reversible redox capability, favorable adsorption of reactants and desorption of resultants are essential for an ideal catalyst. Incorporation of surface hydroxyl over oxide adsorbents was verified as an effective approach for enhanced HCHO adsorption, in which surface OH⁻ could trigger Cannizzaro disproportionation of surface absorbed formaldehyde [2] and provide active H atoms [3] for additional HCHO adsorption. Enhanced oxidation of HCHO was reported by addition of alkali-metal ions to Pt/TiO₂ [17], due to activated H₂O reactivity and catalyzed reaction between surface hydroxyl and formate species.

Heterostructures are capable of providing enhanced physicochemical properties as a result of synergistic combinations of constituent building blocks as well as heterojunctions with unusual functionality. Heterostructures therefore offer enormous opportunities on tailoring functionality by a proper combination of

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components. Construction and utilization of heterostructures have become a research hotspot due to their extraordinary properties and significant application potential [32–42]. Heterostructures such as $\text{MnO}_x\text{-CeO}_2$, [8,15] $\text{TiO}_2\text{-Al}_2\text{O}_3$ [43,44], $\text{Fe}_2\text{O}_3\text{-MnO}_2$ [45], CuO-MnO_2 [45] and $\text{ZrO}_2\text{-poly(ethylene terephthalate)}$ [46] were reported for enhanced room-temperature HCHO oxidation, with trace loading of precious co-catalysts.

Precise modulations of spatial, size and heterointerface in heterostructures are a determining aspect for triggering enhanced functionality and deep understanding the structure-activity correlations. In photocatalysis, proper heterojunctions render effective separation of photo-induced electron-hole pairs [32–38]. In contrast, heterointerfaces containing impurities and/or buffer layers tends to deteriorate spatial separation of photo-induced electron-hole pairs by functioning as recombination centers [34]. Therefore, spatial and size control of each component and interfaces in heterostructures is of importance, which, however, remains a challenge.

Oriented growth is regarded as one of the best protocols to attain a well-defined heterostructure with clean interface [39], in which epitaxial growth of branches over stems offers well-defined growth orientation and minimized cross-contamination in interface. The corresponding heteroepitaxy therefore possesses well-defined spatial and size configurations as well as clean heterointerface. The underlying scientific grounds for controllable construction of the heteroepitaxy lie in establishing facet couples between branches and backbones. For instance, *d*-spacing of (004) plane of hausmannite- Mn_3O_4 (0.23670 nm) is roughly one third of *d*-spacing of (001) plane of layered- MnO_2 (0.70498 nm). Such a facet couple based on crystallographic match endows oriented growth of layered MnO_2 nanosheets over hausmannite- Mn_3O_4 octahedra with exposed {101} facets, in which a clean interface is present [39].

Such a facet coupling is quite common between components with the same dimensions. The corresponding axial and lateral epitaxial growth of one-dimensional (1D) [36,41,42] and two-dimensional (2D) [33,35] heteroepitaxy are proven to be successful and generic. In the above scenario, similar crystallographic configurations in the interface of the 1D/1D and 2D/2D heteroepitaxy facilitate the oriented growth. However, construction of 1D/2D heteroepitaxy remains a challenge, mainly due to the broken crystallographic similarity in heterointerface.

In this contribution, we propose a straightforward strategy to controllable preparation of 1D/2D heteroepitaxy by employing the “rolling-cum-phase transformation” effect. Generally, 2D nanostructures with high surface energy tends to curl and roll into 1D nanostructures, governed by the “rolling-cum-phase transformation” mechanism [47]. The corresponding 1D and 2D nanostructures have inherent facet coupling, which forms the scientific basis for oriented growth between the 1D and 2D counterparts. Such a protocol for preparation of 1D/2D heteroepitaxy (notated as $\alpha\text{-MnO}_2\text{@L-MnO}_2$) is herein demonstrated as oriented growth layered MnO_2 nanosheets (denoted as L- MnO_2) over $\alpha\text{-MnO}_2$ nanotubes. The epitaxial relationship between layered MnO_2 branches and $\alpha\text{-MnO}_2$ backbones is rationalized. After incorporation of trace Pt nanoparticles (i.e. 1 wt%), the $\text{Pt}/\alpha\text{-MnO}_2\text{@L-MnO}_2$ shows enhanced catalytic capability than that of $\text{Pt}/\alpha\text{-MnO}_2$ and $\text{Pt}/\text{L-MnO}_2$ and excellent cycle stability toward room-temperature oxidation of HCHO due to the synergetic combination between each component. Density-Functional-Theory (DFT) simulations indicate that $\alpha\text{-MnO}_2$ has strong adsorption/activation of O_2 and layered- MnO_2 facilitates desorption of H_2O . The present study provides scientific insights on rational designs of affordable and efficient catalysts for thermal catalytic oxidation.

2. Experimental section

The experimental details are provided in the Supporting Information (SI).

The individual $\alpha\text{-MnO}_2$ and L- MnO_2 were prepared by a reported hydrothermal preparation with minor modifications [48,49]. The hybrid MnO_2 ($\alpha\text{-MnO}_2\text{@L-MnO}_2$) was constructed by a facile seed-epitaxial route employing the synthesized $\alpha\text{-MnO}_2$ as seeds [39]. To prepare Pt/ MnO_2 samples, 300 mg MnO_2 powder ($\alpha\text{-MnO}_2$, L- MnO_2 and $\alpha\text{-MnO}_2\text{@L-MnO}_2$) was dispersed in 10 mL deionized (DI) water, and then mixed with 0.8 mL of H_2PtCl_6 solution (0.0193 M) under magnetic stirring. Afterward, 5 mL of the mixed aqueous solutions of NaBH_4 solution (0.572 M), NaOH solution (0.25 M) and sodium citrate solution (1 mM) was quickly added into the suspension under vigorous stirring at 60°C for 1 h. Finally, the sample was washed and centrifuged with DI water, and dried at 60°C for 12 h. The content of Pt in the Pt/ MnO_2 samples is controlled to be 1 wt%. The samples were represented as Pt/ $\alpha\text{-MnO}_2$, Pt/L- MnO_2 and Pt/ $\alpha\text{-MnO}_2\text{@L-MnO}_2$.

Room-temperature removal of HCHO was carried out in a 6 L organic glass box covered by a layer of aluminum foil on its inner wall [14]. 100 mg catalyst powder was dispersed on the bottom of a glass Petri dish with a diameter of 14 cm. After placing the sample-containing dish at the bottom of the reactor with a glass slide cover, 25 μL of formaldehyde solution (CAS No. 50-00-0, 37 wt% in water, contains 10–15% methanol as stabilizer to prevent polymerization) was injected into the reactor with a 5 W fan at the bottom of reactor. The HCHO solution completely volatilized and the concentration of HCHO quickly became stabilized at 300 ± 10 ppm. The adsorption and catalytic oxidation tests were carried out at room temperature ($23 \pm 2^\circ\text{C}$). The relative humidity inside the organic glass box remained unchanged. The relative humidity in the laboratory was near 75%. In the present static experimental setup, it is of challenge to precisely tailor the relative humidity in the reaction box. The influence of relative humidity was previously investigated over Mn–Co–O [26] and Pt/ TiO_2 [27]. The above references suggest that water enhances HCHO oxidation. Therefore, higher relative humidity is beneficial to HCHO oxidation, in which water acts as a promoter to generate more surface hydroxyls and enhance removal of intermediates.

The initial concentration of HCHO was controlled at ~ 300 ppm, which remained constant until the removal of the glass slide cover from the Petri dish to trigger the adsorption or catalytic oxidation reaction of HCHO. The concentrations of CO_2 and HCHO were online recorded using a Photoacoustic IR Multigas Monitor (INNOVA air Tech Instruments Model 1412) to evaluate the adsorption and catalytic performance. In the recycling experiments, no generations were carried out.

Density-Functional-Theory (DFT) calculations were used to investigate surface chemistry of the MnO_2 samples ($\alpha\text{-MnO}_2$ {100} surface and layered- MnO_2 {001} surface). All DFT calculations were performed by CASTEP package on the basis of the plane-wave-pseudo-potential approach. The Perdew-Burke-Ernzerhof (PBE) of the generalized gradient approximation (GGA) was used as the exchange-correlation function. The interaction between valence electrons and ionic core was described by the ultrasoft pseudo-potential. The higher cutoff energy and the wider Monkhorst-Pack *k*-point mesh were tested. The obtained results suggested that the variations were smaller than 0.005 \AA in displacement and 0.005 eV in energy, indicating the high accuracy of present calculations. The calculation smearing on adsorption energy is lower than 0.015 eV , which can satisfy the requirement of theoretical calculation. More information is provided in the SI.

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