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Preparation of hierarchical hollow structures assembled from porous NiCo$_2$O$_4$ nanosheets for diesel soot elimination

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Abstract

Construction of catalysts with designed microstructures is critically important in heterogeneous catalysis. The soot catalytic oxidation was considered as one of the most efficient methods for the diesel soot elimination, but its development has been hindered by the lack of efficient catalysts. The hierarchically porous materials with well-defined microstructures are expected to perform high-catalytic activity for the large-sized soot particulates elimination. Herein, we report a method to prepare a novel hierarchical hollow structure (HHS) assembled from porous NiCo$_2$O$_4$ NSs, referred to as NiCo$_2$O$_4$ HHS. The cation-exchange reaction and Kirkendall effect induce the conversion from the Co-Asp (Asp: aspartic acid) fibers to the Co,Ni-Asp HHSs. The NiCo$_2$O$_4$ HHSs are prepared through annealing the Co,Ni-Asp HHSs. As a proof-of-concept application, the unique NiCo$_2$O$_4$ HHS is used as a catalyst to eliminate the soot particulates and exhibits superior performance, which could be attributed to the improved soot-catalyst contact, sufficient active sites and strong active oxygen species.

KEYWORDS

chemical conversion, hierarchically porous, hollow structure, NiCo$_2$O$_4$, soot elimination

1 | INTRODUCTION

Construction of catalysts with designed microstructures is critically important in heterogeneous catalysis.$^{1-4}$ Soot particulates released from diesel engines give rise to serious environmental and health problems.$^{5,6}$ The combination of diesel particulate filters and soot oxidation catalysts has been considered as one of the most efficient methods for the diesel soot elimination.$^{7,8}$ Therefore, it is desired to develop low-cost, efficient and green catalysts to decrease the ignition temperature of soot particulates.

Although platinum-based precious metals have shown excellent catalytic performance, the scarcity and high-price limit their broad utilization.$^{9,10}$ Recently, numerous cost-effective transition metal oxides, especially those with spinel-like or perovskite-like structures,$^{11-13}$ have been explored and used as soot combustion catalysts. However, the catalytic oxidation of soot particulates is a typical gas-solid-solid tri-phase reaction consisting of gaseous reactants (NO$_x$ and O$_2$), solid reactants (soot particulates) and solid catalyst. The conventional meso-/microporous catalysts are inaccessible for the large-sized soot
particulates (25-100 nm).\textsuperscript{14} To solve this problem, a series of advanced catalysts with macro-porous structures have been developed. For example, by using the hard-template method, Wei et al. synthesized three-dimensional (3D) ordered macro-porous catalysts, which exhibited improved catalytic activity for the soot combustion.\textsuperscript{15} In addition, our previous works demonstrated that the monolithic nanoarray structure could remarkably improve the soot-catalyst contact.\textsuperscript{16} Nevertheless, the relatively small surface area of macro-porous catalysts limits the number of active sites. Therefore, the hierarchically porous materials are expected to perform high-catalytic activity. On the other hand, although two-dimensional (2D) nanosheets (NSs) exhibited high-catalytic performance,\textsuperscript{17-20} their easy aggregation hinders their wide utilization. Fortunately, the assembly of 2D NSs into hollow structures can prevent 2D NSs from aggregation, endowing 2D NSs with promising potential in catalysis.\textsuperscript{21,22}

In this work, we report a method to prepare a novel hierarchical hollow structure (HHS) assembled from porous NiCo$_2$O$_4$ NSs, referred to as NiCo$_2$O$_4$ HHS. As a proof-of-concept application, the unique NiCo$_2$O$_4$ HHS is used as a catalyst to eliminate the soot particulates, which exhibits superior performance.

Figure 1A illustrates the synthetic procedure for the porous NiCo$_2$O$_4$ HHSs. First, the Co-aspartic acid (Co-Asp) fibers were prepared according to our previous work (Figures S1 and S2).\textsuperscript{23-25} The Co,Ni-Asp HHSs made of NSs were obtained by reacting Co-Asp fibers with Ni$^{2+}$ ions for 3 hours (Step 1 in Figure 1A). The scanning electron microscope (SEM) images show the hierarchical nanostructure assembled from 2D NSs with thickness of 12.1 ± 3.4 nm (Figure 1B and Figure S3A). The transmission electron microscope (TEM) image of a single nanostructure reveals its hollow interior and open ends (Figure 1C), indicating the formation of 2D NS-assembled hollow structure. The X-ray diffraction (XRD) pattern confirms the inorganic-organic hybrid crystal structure of Co,Ni-Asp HHSs (Figure S3B). Scanning transmission electron microscope and energy dispersion spectrum

\begin{figure}[h]
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\caption{A, Schematic illustration for preparation of the NiCo$_2$O$_4$ HHS. B, SEM image, C, TEM image, and D, STEM-EDS elemental mappings of the Co,Ni-Asp HHSs. Inset in (B): high-magnification SEM image of Co,Ni-Asp HHSs. E, SEM image, F, TEM image, G, STEM-EDS elemental mappings in the selected area in (F), H, STEM-EDS elemental line scanning, I, nitrogen adsorption/desorption isotherms, and J, XRD pattern of the NiCo$_2$O$_4$ HHSs. Insets in (E): high-magnification SEM image, and (I), mesopore size distribution of the NiCo$_2$O$_4$ HHSs.}
\end{figure}
(STEM-EDS) elemental mapping images exhibit that the elements of Co, Ni, and O are uniformly distributed in the whole hollow structure (Figure 1D). The annealing treatment can induce the decomposition of Co,Ni-Asp HHSs to form porous NiCo$_2$O$_4$ HHSs (Step 2 in Figure 1A). As shown in the SEM images (Figure 1E and its inset), although the hierarchical morphology of NS-based hollow structures maintained well after annealing, mesopores appeared in the NSs with thickness of 10.9 ± 1.9 nm (Figure S4A). The TEM image (Figure 1F) confirms the 2D NS-based hollow structure with open ends. A typical STEM-EDS elemental mapping manifests the homogeneous distribution of Co, Ni, and O in the thermal-induced decomposition product (Figure 1G). The internal cavities are further verified by the STEM-EDS elemental line scanning profiles (Figure 1H). The surface area and size distribution of mesopores (2-50 nm) in the product are determined by nitrogen physisorption. The mesopores with pore size centered at ~7 nm (inset in Figure 1I) were generated in the NSs owing to the thermal decomposition of aspartic acid, providing a specific surface area as high as 213.6 m$^2$/g (Figure 1I). Moreover, the hierarchical structure assembled from 2D NSs endows the NiCo$_2$O$_4$ HHSs with numerous macropores with pore size of 89.7 ± 49.0 nm formed on the surface of HHSs (Figure 1E and Figure S4B). All the XRD peaks can be indexed to the spinel-structured NiCo$_2$O$_4$ (JCPDS No. 20-0781) (Figure 1J). In the Ni 2p X-ray photoelectron spectroscopy (XPS) spectrum (Figure S5A), the peaks at 873.9 and 855.8 eV are assigned to Ni$^{3+}$, while the binding energy at 871.6 and 854.1 eV are indexed to Ni$^{2+}$. In the Co 2p spectrum (Figure S5B), the peaks at 795.1 and 780.1 eV are attributed to Co$^{3+}$, whereas, the peaks centered at 796.7 and 782.8 eV arise from Co$^{2+}$. All the aforementioned results prove the formation of the NiCo$_2$O$_4$ HHSs.

To reveal the conversion from Co-Asp fibers to Co,Ni-Asp HHSs, the intermediates obtained at different reaction time were studied by SEM and TEM (Figure 2). As shown in Figure 2A,B, the surface of Co-Asp fibers is quite smooth. After the Co-Asp fibers reacted with Ni$^{2+}$ ions for 0.5 hour, a thin layer of small NSs were generated on the surface (Figure 2C,D). A Co-Asp fiber@Co,Ni-Asp NS yolk-shell heterostructure was obtained at reaction time of 1 hour (Figure 2E,F). When the reaction was stopped at 3 hours, the Co-Asp fibers have been fully converted into the Co,Ni-Asp HHSs (Figure 2G,H). A possible mechanism involving the cation-exchange reaction and Kirkendall effect is proposed for formation of the Co,Ni-Asp HHSs (Figure 2I).

**FIGURE 2** A, C, E, G, SEM, and B, D, F, H, TEM images of the obtained products after the Co-Asp fibers reacted with Ni$^{2+}$ at different reaction time: A and B, 0 hour, C and D, 0.5 hour, E and F, 1 hour, and G and H, 3 hours. I, Schematic illustration of the conversion from the Co-Asp fiber to the Co,Ni-Asp HHS.
First, Ni²⁺ ions can quickly exchange with Co²⁺ ions of Co-Asp fibers (Figure 2A,B) to produce a thin layer of Co,Ni-Asp shell on the surface of the Co-Asp fiber (Figure 2C,D). The concentration gradient of metal ions can drive the outward diffusion of Co²⁺ ions and the inward diffusion of Ni²⁺ ions. The difference of the diffusion rates between Co²⁺ and Ni²⁺ ions (ie, Kirkendall effect) lead to the yolk-shell intermediate (Figure 2E,F). When the interior Co-Asp is completely consumed, the Co,Ni-Asp HHS is obtained (Figure 2G,H).

As a proof-of-concept application, the Co,Ni-Asp HHSs were used as catalyst to eliminate the soot particulates. The catalytic soot combustion was evaluated by temperature programmed oxidation (TPO). As comparison, the disorder NiCo₂O₄ NSs were prepared (Figure S6) and also used as catalyst for the soot combustion. As shown in Figure 3A, the NiCo₂O₄ HHSs exhibit higher activity than NiCo₂O₄ NSs. Compared with the NiCo₂O₄ NSs, the \( T_{10} \) value, that is, the temperature at 10% soot conversion, decreases from 330°C to 321°C using NiCo₂O₄ HHSs as catalyst, and the \( T_{50} \) value, that is, the temperature at 50% soot conversion, decreases from 379°C to 354°C (Figure 3B), which is among the best in the soot elimination catalysts (Table S1). It is worth mentioning that the practical temperature when diesel engines exhaust is in the range of 150°C to 380°C. Therefore, the NiCo₂O₄ HHSs can catalytically remove soot particulates at the practical exhaust temperature. As known, NO₂ is a strong oxidizer and can be reduced by soot particulates. In order to reveal the role of NO₂ (NO + NO₂) in combustion of soot particulates, the NOₓ concentration was in situ monitored. As a result, the NO concentration decreases more (Figure 3C), and the NO₂ concentration increases more using the NiCo₂O₄ HHSs as catalyst compared to the NiCo₂O₄ NSs (Figure 3D), revealing that the NiCo₂O₄ HHSs can more efficiently catalyze the oxidation of NO to NO₂. It is worth mentioning that the temperature corresponding to the maximum NO₂ concentration (319°C, Figure 3C,D) is very close to the ignition temperature of soot using NiCo₂O₄ HHSs (321°C, Figure 3B). Therefore, it is reasonable to indicate that the removal of soot is accompanied by the reduction of NO₂.

Based on the aforementioned results, the soot oxidation process using the NiCo₂O₄ HHSs is illustrated (Figure 4A). Soot particulates are first captured by the 2D NSs of NiCo₂O₄ HHSs (Step 1 in Figure 4A and Figure S7). After NO is oxidized to NO₂ on the surface of
NiCo$_2$O$_4$ HHSs, both NO$_2$ and O$_2$ oxidize the soot into CO$_2$ (Step 2 in Figure 4B). To further explain the high activity of the NiCo$_2$O$_4$ HHSs, XPS and temperature programmed reduction by soot (soot-TPR) were performed. The O 1s peak in the XPS (Figure 4B and Figure S8) showed that the oxygen adsorbed on the surface of the NiCo$_2$O$_4$ HHSs are much more compared to that of the NiCo$_2$O$_4$ NSs. Moreover, there are mainly two reductive peaks of $\alpha$ and $\beta$ in the soot-TPR (Figure 4C). The $\alpha$ peak represents the active oxygen species for the soot elimination. Compared with the NiCo$_2$O$_4$ NSs, the $\alpha$ peak in the NiCo$_2$O$_4$ HHSs appears at lower temperature, indicating its stronger oxidation ability. Moreover, there is no obvious change of the morphology, structure and chemical state of the NiCo$_2$O$_4$ HHSs after the TPO test (Figure 1E,J, Figures S5 and S9), indicating their high stability. Therefore, the high activity and stability for the catalytic soot elimination can be ascribed to the unique hierarchical nanostructure of the NiCo$_2$O$_4$ HHSs.

In summary, we have successfully synthesized the NiCo$_2$O$_4$ HHSs. The cation-exchange reaction and Kirkendall effect induce the conversion from the Co-Asp fibers to the Co,Ni-Asp HHSs. The NiCo$_2$O$_4$ HHSs are prepared through annealing the Co,Ni-Asp HHSs. The as-obtained NiCo$_2$O$_4$ HHSs exhibit high activity for the catalytic elimination of soot particulates, which could be attributed to the improved soot-catalyst contact, sufficient active sites and strong active oxygen species.

2 | EXPERIMENTAL SECTION

2.1 | Synthesis of Co-aspartic acid (Co-Asp) fibers

In a typical procedure, 3 mmol of Co(NO$_3$)$_2$·6H$_2$O, 3 mmol of L-aspartic acid, and 3 mL of NaOH (2 M) aqueous solution were added to a mixture of 15-mL deionized water and 18-mL glycol. After vigorous stirring for 1 hour, the solution was transferred into a 50-mL Teflon-lined autoclave, and then heated and maintained at 180°C for 5 hours. The pink precipitate was collected by centrifugation at 3000 rpm for 10 minutes, and dried at 40°C for 12 hours.

2.2 | Synthesis of the Co,Ni-Asp hierarchical hollow structures (Co,Ni-Asp HHSs)

The as-prepared Co-Asp fibers (0.075 g) were dispersed in 20 mL ethanol. Then, 10 mL of Ni(NO$_3$)$_2$·6H$_2$O
(0.1 mol L\(^{-1}\)) aqueous solution were injected into the Co-Asp fiber ethanolic solution with constant stirring. The mixed solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave, and then heated and maintained at 180°C for 3 hours. The blue-green precipitates were collected by centrifugation at 3000 rpm for 10 minutes, and dried at 40°C for 12 hours.

2.3 | Synthesis of the NiCo\(_2\)O\(_4\) hierarchical hollow structures (NiCo\(_2\)O\(_4\) HHSs)

The NiCo\(_2\)O\(_4\) HHSs were prepared by annealing Co,Ni-Asp HHSs in air at 400°C for 4 hours.

2.4 | Synthesis of NiCo\(_2\)O\(_4\) nanosheets (NiCo\(_2\)O\(_4\) NSs)

1.25 mmol of nickel chloride (NiCl\(_2\)) were first dissolved in 500-mL deionized water, and then 2.5 mmol of cobalt chloride (CoCl\(_2\)·6H\(_2\)O) and 45 mmol of hexamethylenetetramine (HMT, 99%, Sigma-Aldrich) were added. The mixed solution was refluxed at 95°C for 5 hours under continuous magnetic stirring and N\(_2\) atmosphere. The powder was collected by centrifuging at 3000 rpm for 10 minutes. Then, the NiCo\(_2\)O\(_4\) NSs were obtained by annealing the powder in air at 400°C for 4 hours.

2.5 | Characterization

The scanning electron microscopy (SEM) images were taken with a Hitachi S-4800 scanning electron microscope (SEM, 3 kV). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS) elemental line scanning, and STEM-EDS elemental mapping were obtained with FEI Tecnai F2F20 system equipped with GIF863 Tridiem (Gatan). The X-ray diffraction (XRD) patterns were recorded with Bruker D8 Focus Diffraction System using a Cu Ka source (\(\lambda = 0.15406 \text{ nm}\)). The surface area and pore size distributions were determined by nitrogen physisorption by a NOVA 2200e system. The surface area was calculated using the Brunauer-Emmett-Teller method. Pore size distributions were calculated using the Barrett-Joyner-Halenda method from the desorption branch. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a spectrometer having Al KR radiation (PHI5000 Versa Probe). Fourier Transform Infrared Spectroscopy (FTIR) spectra were recorded on a MAGNA-IR 750 (Nicolet Instrument Co.). The temperature programmed reduction by soot (soot-TPR) was evaluated by the thermogravimetry (TG) technique using Printex-U purchased from Degussa as the model soot. The mixture was heated from 200°C to 850°C at a heating rate of 10°C min\(^{-1}\) in an atmosphere of N\(_2\) with a flow rate of 50 mL min\(^{-1}\).

2.6 | Catalytic activity evaluation

The temperature programmed oxidation (TPO) of soot was performed using a fixed-bed tubular quartz reactor (Ø = 8 mm). The Printex-U purchased from Degussa was used as the model soot. Catalyst and soot were blended using an agate mortar, and then placed into the center of a quartz reactor. The weight ratio of catalyst to soot is 10:1. The mixture of catalyst and soot was heated from 200°C to 600°C at a heating rate of 2°C min\(^{-1}\) in the flowing N\(_2\) atmosphere (50 mL min\(^{-1}\)) containing 650 ppm NO and 5% O\(_2\). The composition of the effluent gas was analyzed by a Chemiluminescence NO-NO\(_2\)-NO\(_x\) Analyzer (42i-HL, Thermal Scientific) and on-line gas chromatograph (BFS, SP3430) using a flame ionization detector (FID). The catalytic activity was evaluated by the values of \(T_{10}\) and \(T_{50}\), which are defined as the temperatures at the soot conversions of 10% and 50%, respectively. \(T_{10}\) was chosen as the ignition temperature for soot particulates.

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