Supporting Information

Controlled Synthesis of Hierarchically Crossed Metal Oxide Nanosheet Arrays for Diesel Soot Elimination

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EXPERIMENTAL SECTION

All chemicals were of analytical grade and used as received without further purification. Aqueous solutions were prepared using distilled water.

Preparation of the FeOx substrate

In a typical procedure, one piece of iron foil (2 cm × 2 cm × 0.05 cm) was sonicated in acetone, ethanol and distilled water, sequentially. After drying under N2 atmosphere, the as-obtained iron foil was placed in alumina boat, which was immediately heated to 500 °C in a muffle furnace. After calcination for 4 h, the FeOx substrate was prepared.

Preparation of hierarchically crossed metal oxide (MO, M=Co, Ni, Mg) nanosheet array on FeOx substrate

Firstly, the FeOx substrate was dipped into 100 mL 0.1 M M(NO3)3·nH2O (M=Co, Ni, Mg) aqueous solution. After impregnation for 1 h, the sample was taken out with a tweezer and dried at 120 °C for 15 min. Then, the sample was calcined at 350 °C for 30 min in air to finish the first loading cycle. The loading cycle was repeated for 4 times to obtain the metal oxide crossed nanosheet array on FeOx substrate.

In addition, the sample of Co3O4 with 2 times of loading cycle (Table S1) was also synthesized for comparison study.

Preparation of hierarchically crossed composite metal oxide (CoBa2O4 and CoMg2O4) nanosheet array on FeOx substrate

The preparation process of the hierarchically crossed composite metal oxide nanosheet array on FeOx substrate was the same as the crossed Co3O4 nanosheet array on FeOx substrate.
described above except that the cobalt nitrate precursor solution was replaced by mixed metal nitrates solution. The details of reaction conditions for the preparation of composite metal oxide crossed nanosheet array were displayed in Table S1.

**Preparation of Co$_3$O$_4$ nanoparticles on Si and TiO$_2$ substrates**

The preparation procedure was the same as that for Co$_3$O$_4$ crossed nanosheet array/FeO$_x$ substrate except for the substrate.

**Characterization:** The scanning electron microscopy (SEM) images were taken with a Hitachi S-4800 scanning electron microscope (SEM, 5 kV). Transmission electron microscopy (TEM) images were obtained with JEOL-2100F system equipped with EDAX Genesis XM2. The X-ray diffraction (XRD) patterns of the samples were recorded on Bruker D8 diffraction meter using Cu Kα (λ= 0.15418 nm) as radiation source. Raman experiments were performed on Invia Reflex spectrometer of RENISHAW Company. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a VG ESCALAB 220i-XL system. The C1s peak was used as the reference to calibrate the XPS spectra. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out on a Perkin-Elmer Diamond TG/DTA instrument.

**Activity evaluation**

The catalytic activities of the samples for soot combustion were evaluated by the TG/DTA technique using Printex-U soot (Degussa) as the model reactants. The mix of catalysts and soot particulates was achieved by deposition contact mode according to our previous works.$^{1-3}$ First, the soot was dispersed in ethanol under ultrasonic assistance. In the next step, the produced suspension was dropped on the surface of the monolithic catalysts and dried at 60 °C. The weight ratio of soot to catalyst is 1:20. The mixture of soot and catalyst were then heated from room temperature to 650 °C at a slope of 5 °C min$^{-1}$ in an atmosphere of 600 ppm NO, 10 vol % O$_2$ and balanced N$_2$ with a flow rate of 50 mL min$^{-1}$. After the temperature-programmed oxidation experiment, a DTG curve with a complete weight loss peak was obtained. In this work, $T_m$, defined as the temperature at which the soot was oxidized with the maximal rate, was used to evaluate the performance of the catalysts.
Table S1 Details of the reaction conditions for the fabrication of hierarchically crossed MO nanosheet array on FeOₓ substrate.

<table>
<thead>
<tr>
<th>Material</th>
<th>M(NO₃)ₓ·nH₂O solution (0.1 M, Total Content)</th>
<th>Times of loading cycle</th>
<th>Mole ratioa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₃O₄</td>
<td>Co(NO₃)₂·6H₂O</td>
<td>2</td>
<td>1:1.2 (Co:Fe)</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>Co(NO₃)₂·6H₂O</td>
<td>4</td>
<td>1:0.32 (Co:Fe)</td>
</tr>
<tr>
<td>NiO</td>
<td>Ni(NO₃)₂·6H₂O</td>
<td>4</td>
<td>1:0.41 (Ni:Fe)</td>
</tr>
<tr>
<td>MgO</td>
<td>Mg(NO₃)₂·6H₂O</td>
<td>4</td>
<td>1:0.63 (Mg:Fe)</td>
</tr>
<tr>
<td>Co₉BaO₄</td>
<td>9Co(NO₃)₂·6H₂O:1Ba(NO₃)₂</td>
<td>4</td>
<td>1:0.07:0.34(Co:Ba:Fe)</td>
</tr>
<tr>
<td>Co₉BaO₄</td>
<td>9.5Co(NO₃)₂·6H₂O:0.5Ba(NO₃)₂</td>
<td>4</td>
<td>1:0.03:0.37(Co:Ba:Fe)</td>
</tr>
<tr>
<td>CoMgO</td>
<td>9Co(NO₃)₂·6H₂O:1Mg(NO₃)₂·6H₂O</td>
<td>4</td>
<td>1:0.06:0.22(Co:Mg:Fe)</td>
</tr>
</tbody>
</table>

a: The mole ratio of different elements is obtained through EDX results; b: The sample is prepared to investigate the formation mechanism of crossed MO nanosheets array; c: The sample is prepared to demonstrate the adjustability of different components in the composite metal oxide.

Fig. S1 The side-view SEM images of the FeOₓ substrate.
Fig. S2 TEM image and the corresponding EDX spectrum of Co$_3$O$_4$ crossed nanosheet array peeled off from FeO$_x$ substrate by sonication.

![EDX spectrum](image)

Fig. S3 (a) Raman spectrum of Co$_3$O$_4$ crossed nanosheet array/FeO$_x$ substrate. (b) XRD patterns of the FeO$_x$ substrates (black line) and Co$_3$O$_4$ crossed nanosheet array/FeO$_x$ substrate (red line). As shown in Fig. S3a, the Raman peaks at 187, 462, 517, 685 cm$^{-1}$ correspond to the $F_{2g}$, $E_g$, $F_{2g}$ and $A_{1g}$ modes of Co$_3$O$_4$. XRD patterns in Fig. S3b (black line) proved that the FeO$_x$ substrate was composed of Fe$_2$O$_3$ (JCPDS 33-0664) and Fe$_3$O$_4$ (JCPDS 65-3107). The Co$_3$O$_4$ (JCPDS 42-1467) was detected after thermal decomposition of cobalt nitrate on FeO$_x$ substrate (red line in Fig. S3b), which is consistent with the Raman result.
**Fig. S4** The digital photographs of the same piece of (a) Fe foil, (b) FeO\(_x\) substrate and (c) Co\(_3\)O\(_4\) crossed nanosheet array/FeO\(_x\) substrate with the size of 2 cm × 2 cm. The digital photograph of (d) Co\(_3\)O\(_4\) crossed nanosheet array/FeO\(_x\) substrate with the size of 5 cm × 5 cm.

**Fig. S5** TEM images and the corresponding EDX spectra of (a) NiO, (b) MgO, (c) CoMg\(_x\)O\(_y\) and CoBa\(_x\)O\(_y\) crossed nanosheet array peeled off from FeO\(_x\) substrate.
**Fig. S6** SEM images of cobalt nitrate on (a) Si and (b) TiO$_2$ substrates.

**Fig. S7** SEM images of Co$_3$O$_4$ on (a) Si and (b) TiO$_2$ substrates.

**Fig. S8** SEM image of Co$_3$O$_4$ crossed nanosheet array/FeO$_x$ substrate after catalysis evaluation for soot elimination.
Fig. S9 XPS spectra of Co$_3$O$_4$ crossed nanosheet array/FeO$_x$ substrate before (upper) and after (lower) catalysis evaluation for soot elimination: (a) survey scan XPS spectra, (b) Co 2p deconvolution spectra, (c) Fe 2p deconvolution spectra, (d) O 1s deconvolution spectra.

References