Electronic Supplementary Information

Catalytically converting the NOx by difunctional Ni-Ga based oxides catalyst

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Fig. S1. TEM images for the as-prepared samples. (a) NiGa$_2$O$_4$. (b) Ni$_{0.5}$Zn$_{0.5}$Ga$_2$O$_4$. (c) Ni$_{0.1}$Zn$_{0.9}$Ga$_2$O$_4$. (d) ZnGa$_2$O$_4$. (b) ZnGa$_2$O$_4$. 

![TEM images](image_url)
Fig. S2. \( \text{N}_2 \) adsorption-desorption measurement. (a)\( \text{NiGa}_2\text{O}_4 \).(b) \( \text{ZnGa}_2\text{O}_4 \).(c) \( \text{Ni}_{0.9}\text{Zn}_{0.1}\text{Ga}_2\text{O}_4 \). The inset shows the pore diameter distribution.

Fig. S3. TEM images for the as-prepared \( \text{Ni}_{0.9}\text{Zn}_{0.1}\text{Ga}_2\text{O}_4 \) sample. Inset shows the the FFT pattern obtained from the HRTEM image. From the FFT pattern, wen can know that the (311) and (111) were the possibly exposed facets.

To demonstrate the possible exposed facets, the FFT pattern was obtained from the HRTEM image, as shown in Fig.S3. Noting that the crystal structure of Ni-Ga based catalyst is cubic, the facets could be identified by combining the two prior knowledge by indexing the corresponding FFT spots.
Fig. S4. Experimental and theoretical results for valence state change of Ni. (a) UV-vis light absorption spectra for Ni$_{0.1}$Zn$_{0.9}$Ga$_2$O$_4$ before and after heating at 300°C in NO. (b) Calculated UV-vis light absorption spectra for ZnGa$_2$O$_4$ before and after Ni partly replacing Ga (denoted as Ni$_{Ga}^{3+}$-ZnGa$_2$O$_4$).

The UV-Vis absorption spectra for the as-prepared Ni$_{0.9}$Zn$_{0.1}$Ga$_2$O$_4$ before and after heating at 300°C in NO were shown in Fig. S2a. After heating in NO, the light absorption edge of the Ni$_{0.1}$Zn$_{0.9}$Ga$_2$O$_4$ exhibited the obvious red-shift. The theoretical calculation method was used to confirm the nature of light absorption edge shift. The NiGa$_2$O$_4$ is a largely inverse spinel with about 92% of Ni$^{2+}$ in the octahedral sites. In NiGa$_2$O$_4$, cations are distributed on tetrahedrally and octahedrally coordinated sublattices. Therefore, for simplification, the normal spinel ZnGa$_2$O$_4$ was used as a model compound to carry out the theoretical calculations. A theoretical model was constructed by Ni partly replacing Ga with a valence state change from Ni$^{2+}$ to Ni$^{3+}$ in ZnGa$_2$O$_4$ to explore the effect of the valence state change of Ni on the light absorption of Zn-modified NiGa$_2$O$_4$. The theoretical calculations indicated that after Ni replacing Ga with a valence state change from Ni$^{2+}$ to Ni$^{3+}$ in ZnGa$_2$O$_4$ the light absorption edge of ZnGa$_2$O$_4$ also presented a similar red-shift. Thus, we can concluded that Ni$^{2+}$ is easier to be oxidized to Ni$^{3+}$ (lose an electron) when occupying the octahedral sites such as in NiGa$_2$O$_4$, which is a largely inverse spinel with about 92% of Ni$^{2+}$ in the octahedral sites.
Fig. S5. In-situ XPS analysis for Ni$_{0.9}$Zn$_{0.1}$Ga$_2$O$_4$ at room temperature and after heating at 300°C in NO. (a) Ga 3d. (b) Ni 2p. (c) Zn 2p. (d) O 1s.