

## Electronic Supplementary Information

### Catalytically converting the NO<sub>x</sub> by difunctional Ni-Ga based oxides catalyst

*Shicheng Yan<sup>a,b\*</sup>, Zhaochun Wu<sup>c</sup>, Qian Xu<sup>a</sup>, Jia Jia Wang<sup>a,b</sup>, Jinhua Hong<sup>d</sup>, Jixue Li<sup>d</sup>,*

*Peng Wang<sup>a</sup>, Zhigang Zou<sup>a,b,c</sup>*

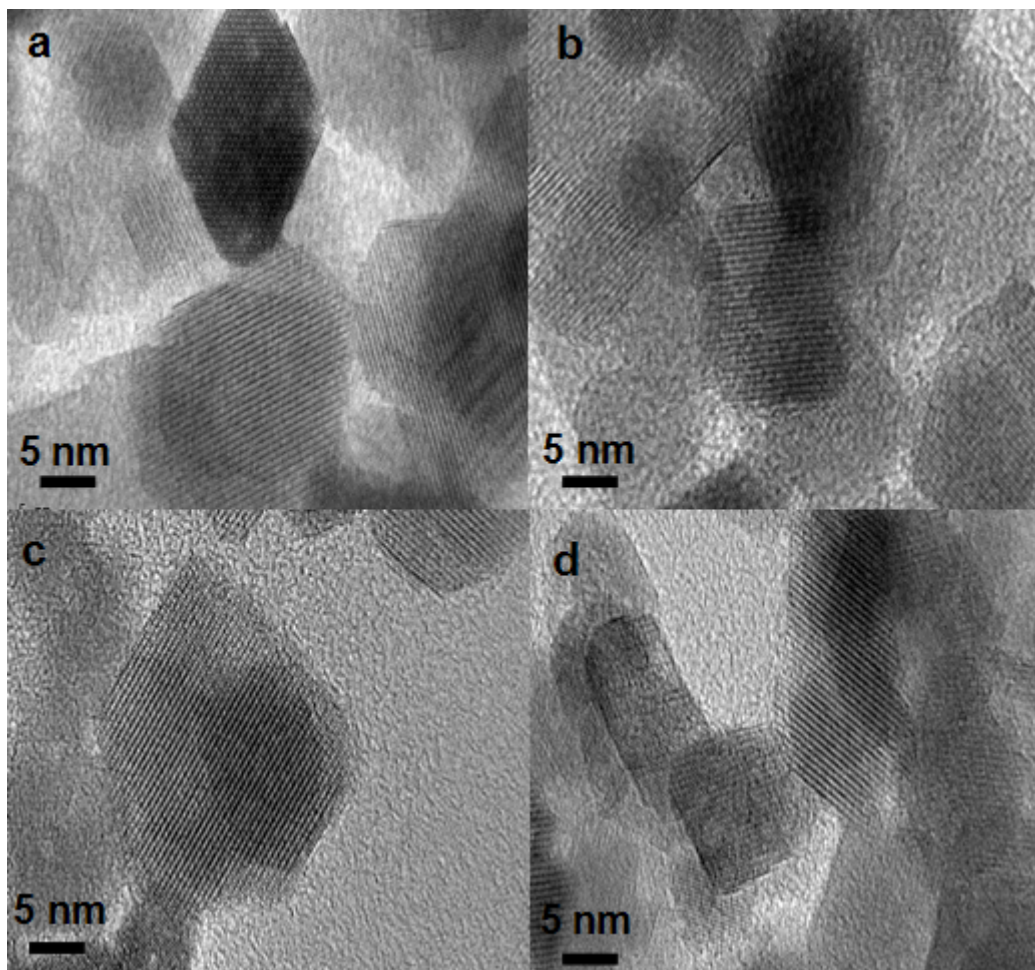
<sup>a</sup>National Laboratory of Solid State Microstructures, Collaborative Innovation Center of Advanced Microstructures, College of Engineering and Applied Sciences, Nanjing University, NO. 22, Hankou Road, Nanjing, Jiangsu 210093, P.R.China

<sup>b</sup>Eco-Materials and Renewable Energy Research Center (ERERC), College of Engineering and Applied Sciences, Nanjing University, NO. 22, Hankou Road, Nanjing, Jiangsu 210093, P.R.China, E-mail: [yscfei@nju.edu.cn](mailto:yscfei@nju.edu.cn)

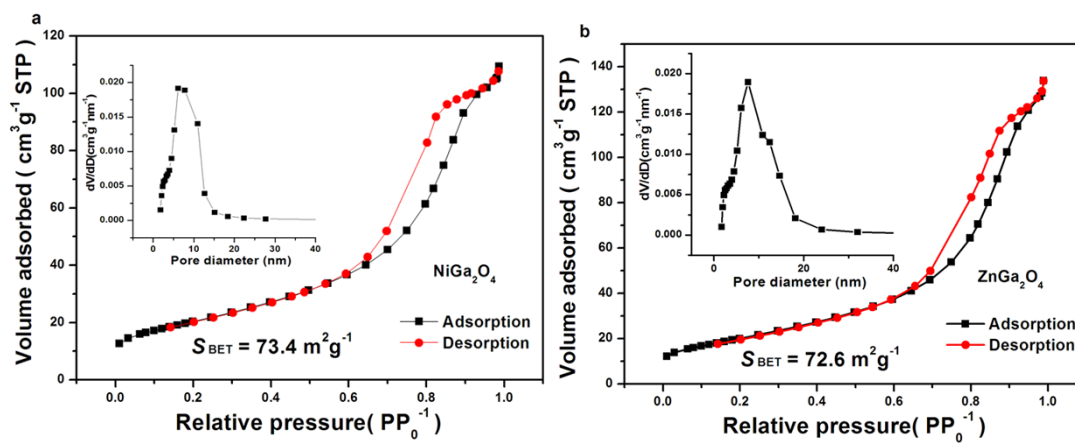
<sup>c</sup> School of Physics, Nanjing University, NO. 22, Hankou Road, Nanjing, Jiangsu 210093, P.R.China

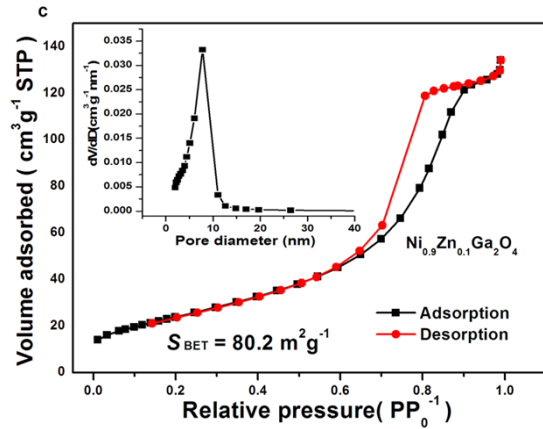
<sup>d</sup>Department of Materials Science and Engineering, Zhejiang University, No.38, Zheda Road, Hangzhou, Zhejiang 310027, P. R. China.

\*To whom correspondence should be addressed. E-mail: [yscfei@nju.edu.cn](mailto:yscfei@nju.edu.cn)

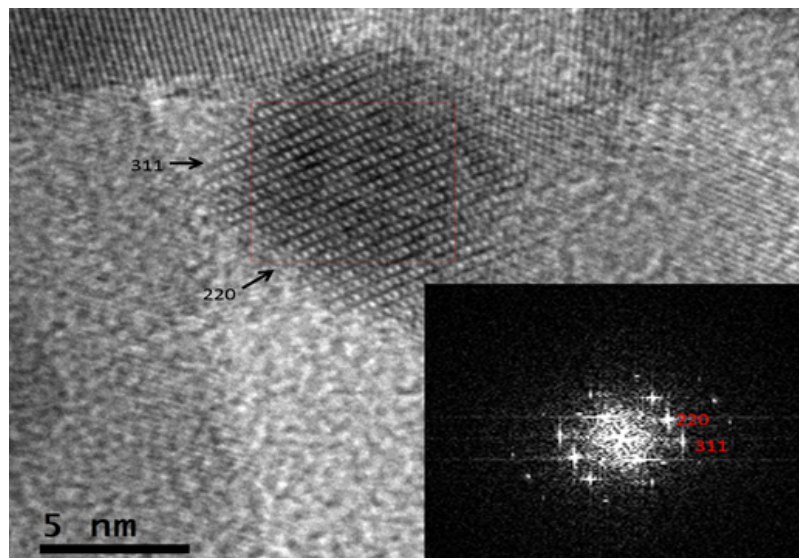


**Fig. S1. TEM images for the as-prepared samples. (a)  $\text{NiGa}_2\text{O}_4$ . (b)  $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Ga}_2\text{O}_4$ . (c)  $\text{Ni}_{0.1}\text{Zn}_{0.9}\text{Ga}_2\text{O}_4$ . (d)  $\text{ZnGa}_2\text{O}_4$ .**



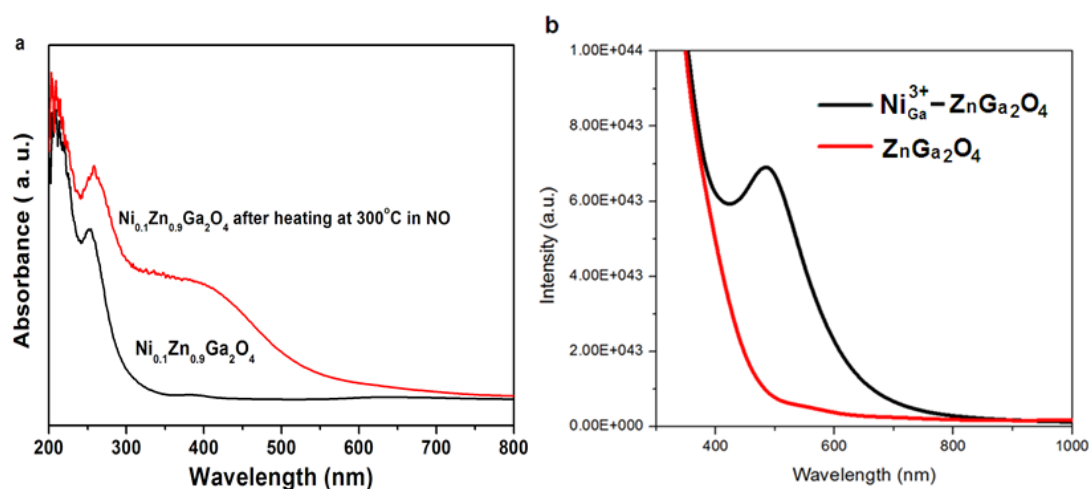


**Fig. S2.**  $\text{N}_2$  adsorption-desorption measurement. (a)  $\text{NiGa}_2\text{O}_4$ . (b)  $\text{ZnGa}_2\text{O}_4$ . (c)  $\text{Ni}_{0.9}\text{Zn}_{0.1}\text{Ga}_2\text{O}_4$ . The inset shows the pore diameter distribution.



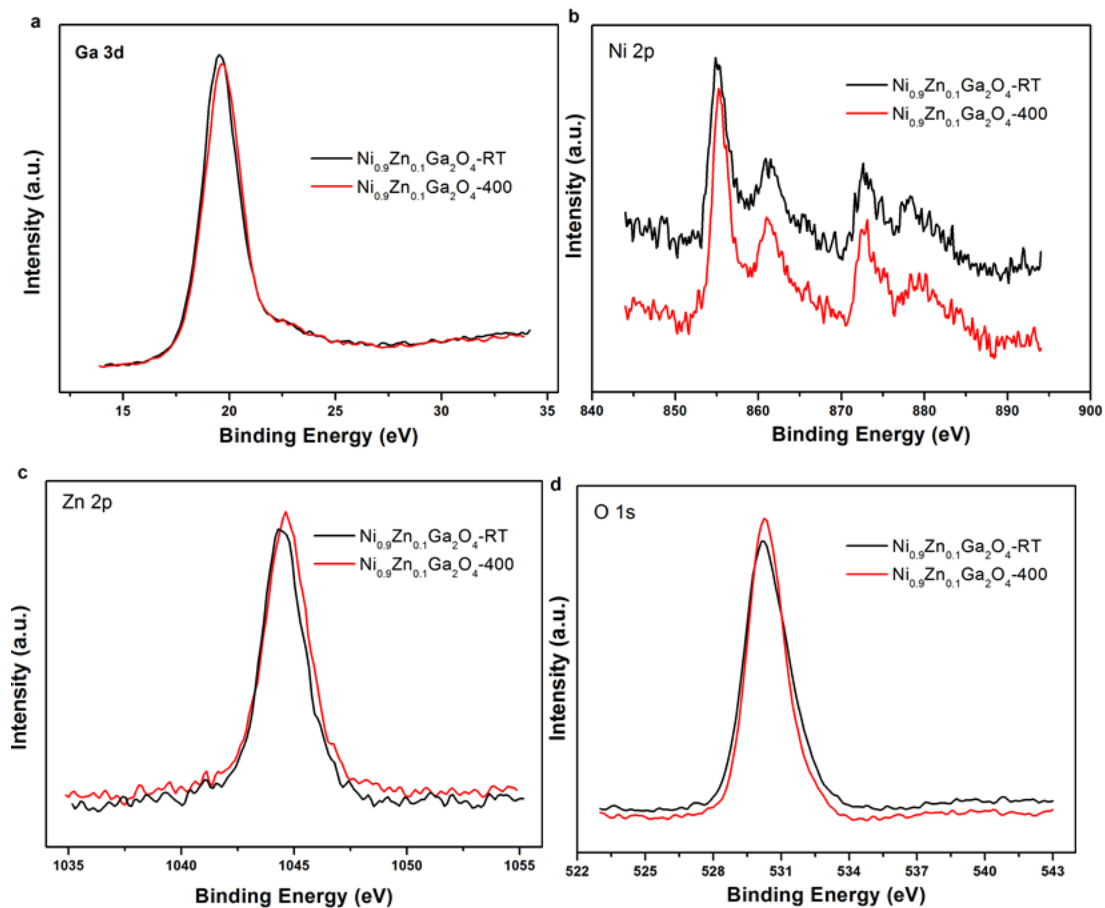
**Fig. S3.** TEM images for the as-prepared  $\text{Ni}_{0.9}\text{Zn}_{0.1}\text{Ga}_2\text{O}_4$  sample. Inset shows the the FFT pattern obtained from the HRTEM image. From the FFT pattern, we can know that the (311) and (111) were the possibly exposed facets.

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  $\text{Ni}_{0.1}\text{Zn}_{0.9}\text{Ga}_2\text{O}_4$  before and after heating at 300°C in NO. (b) Calculated UV-vis light absorption spectra for  $\text{ZnGa}_2\text{O}_4$  before and after Ni partly replacing Ga (denoted as  $\text{Ni}_{\text{Ga}}^{3+}\text{-ZnGa}_2\text{O}_4$ ).

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



**Fig. S5. In-situ XPS analysis for  $\text{Ni}_{0.9}\text{Zn}_{0.1}\text{Ga}_2\text{O}_4$  at room temperature and after heating at 300°C in NO. (a) Ga 3d. (b) Ni 2p. (c) Zn 2p. (d) O 1s.**