Supplementary Information

Enhanced ethanol sensing performance of porous ultrathin NiO nanosheets with neck-connected networks

Changhui Zhao, Jiecai Fu, Zhenxing Zhang and Erqing Xie*

*Corresponding author.

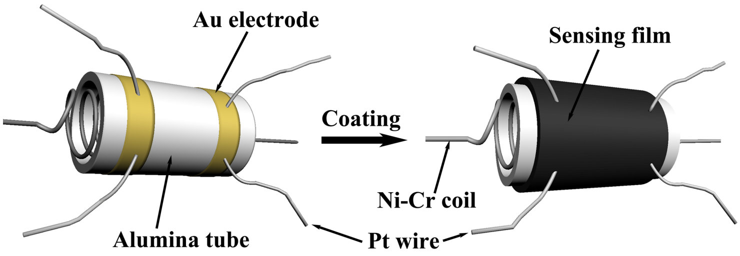

Fig. S1 Schematic illustration of the gas sensor.

Sensor preparation: As-prepared NiO products were mixed with appropriate amount binder (ethyecellulose: terpinol = 10: 90 wt. %) to form a paste and then coated on an alumina tube (as shown in Fig. S1). A pair of gold electrodes was formed at each end of the alumina tube, and each electrode was connected with two platinum wires. The thickness of the sensing film was ~ 200 μm. All of the sensors were dried at 80 °C for 4h before calcined at 350 °C for 2 h to remove any residual organics. The operating temperature was controlled by a heating component, using a Ni-Cr alloy coil heater to insert the alumina tube.

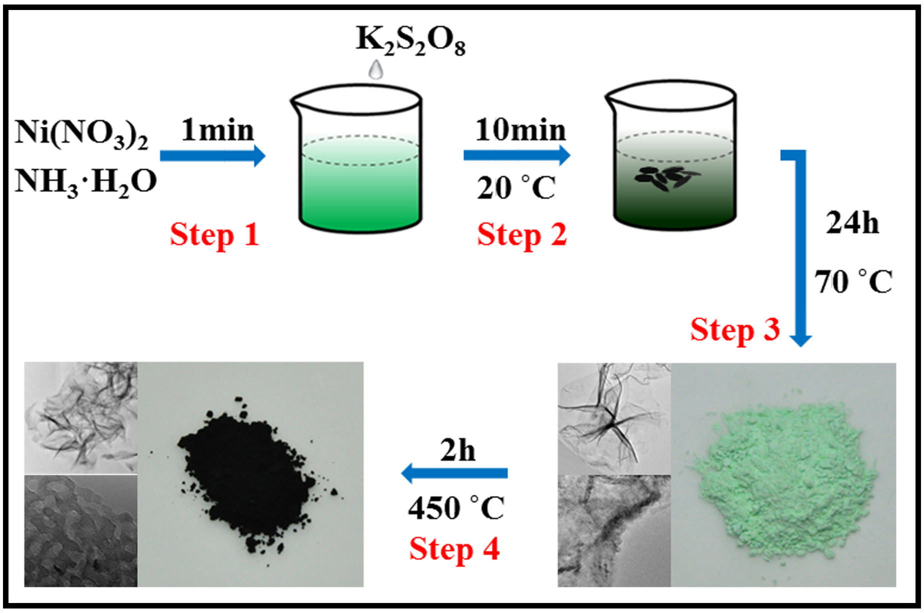

Fig. S2 A formation process of $Ni(OH)_2$ precursors and porous NiO nanosheets.

Formation process of porous NiO nanosheets: The schematic illustration of the porous NiO nanosheets formation process was present in Fig. S2. Previously, lots of work has been done to explain the formation mechanism of porous NiO films for CBD process, and the reaction of CBD was divided into two steps as follows[1]:

$[Ni(H_2O)_{6-x}(NH_3)_x]^{2+} + 2OH^- \rightarrow Ni(OH)_2 + (6-x)H_2O + xNH_3$ (Step 1)

$2Ni(OH)_2 + S_2O_8^{2-} \rightarrow 2NiOOH + 2SO_4^{2-} + 2H^+$ (Step 2)

It was easy nucleation at the surface of stirrer or inter-wall of the beaker in a supersaturated solution at first, then the formed nuclei fell off and homogeneous growth in solutions under the effect of potassium persulfate. However, the formation of sheet structure was attributed to the self-assembly of adjacent particles, which tended to share a common crystallographic orientation to form the lamellar structures, for reducing surface free energy.[2]

The black precipitates were dried at 70 °C for 24 h and turned into green powders (Step 3), and this might be explained by a redox reaction of NiOOH with assist of residual ethanol. The XRD pattern shows that the powders are β-$Ni(OH)_2$ and no NiOOH peaks are observed, which is unambiguous evidence of the reaction. Otherwise, when we applied vacuum suction filtration to separate black precipitates, the precipitates could keep itself color (black) at room temperature. The surface of $Ni(OH)_2$ nanosheets is smooth and nonporous. During the thermal treatment process at 450 °C for 2 h, $Ni(OH)_2$ gradually decomposes into NiO (Step 4). The formation of nanopores is attributed to the loss of water: $Ni(OH)_2 \rightarrow NiO + H_2O$. With the decomposition of big grains, the grain boundaries divide and move to the opposite directions, thus nanopores form. According to XRD results, the average grain size reduces from 23.9 nm to 5.8 nm after calcination. Herein, we adopted a slow heating process at a rate of 1 °C/min to ensure the formation of uniform nanopores and maintain the morphology.

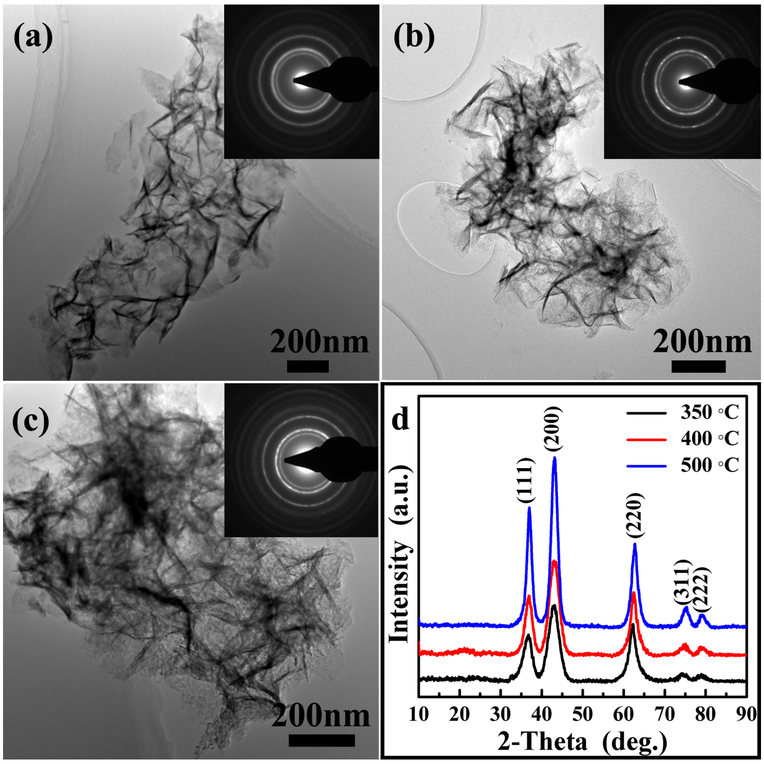

Fig. S3 (a-c) TEM images (the insert is SAED image) and (d) XRD patterns of NiO nanosheets calcined at different temperatures for 2h. (a) 350 °C, (b) 400 °C, and (c) 500 °C.

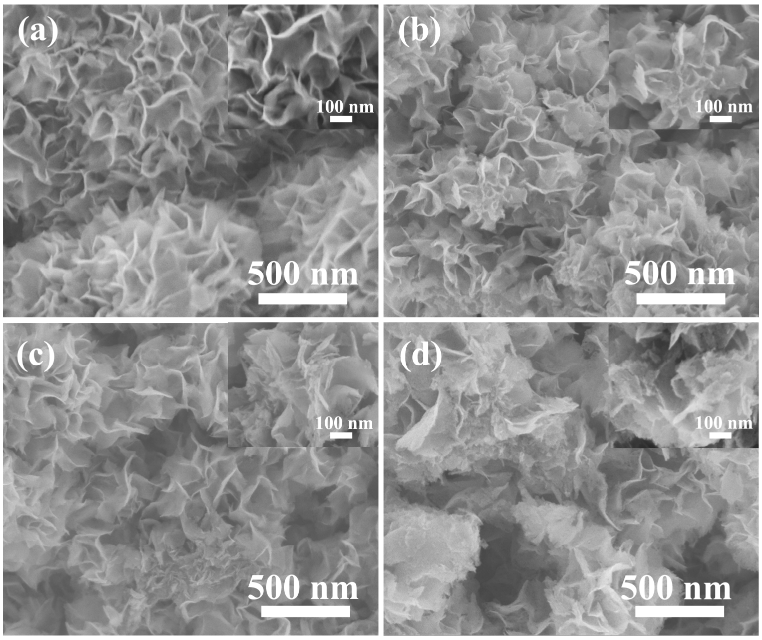

Fig. S4 FE-SEM images (the insert is magnified image) of NiO nanosheets at different calcination temperatures. (a) 350 °C, (b) 400 °C, (c) 450 °C and (d) 500 °C.

Characterization: The changes of NiO nanosheets calcined at 350, 400 and 500 °C were also characterized by TEM and XRD (Fig. S3). All the insetted SAED rings show good crystallinity and agree well with the spacing of the (111), (200), (220), (311), (222), and (400) planes of cubic NiO, respectively. Fig. S3d shows that all X-ray diffraction peaks become sharper and stronger with the increase of calcination temperature, which can be in line with SAED patterns. In Fig. S4, it can be seen that almost all of the nanosheets have nonporous surface and blurred edge (thicker than 5 nm), which is attribute to lower spatial resolution of FE-SEM (compared to HADDF-STEM image in Fig. 1e). However, the difference of nanostructures between nanosheets, at different calcination temperatures, is obvious. It is seriously collapsed and agglomerated at 500 °C, and which is used as a supplement of TEM images.

References:

1. S. Y. Han, D. H. Lee, Y. J. Chang, S. O. Ryu, T. J. Lee and C. H. Chang, *J. Electrochem. Soc.*, 2006, **153**, C382-C386.
2. X. Xia, J. Tu, Y. Zhang, X. Wang, C. Gu, X. Zhao and H. J. Fan, *ACS nano*, 2012, **6**, 5531-5538.