

Supporting Information

Of

Bimetal Pd/Ni functionalized WO₃ nanospheres for sensitive low-concentration hydrogen detection

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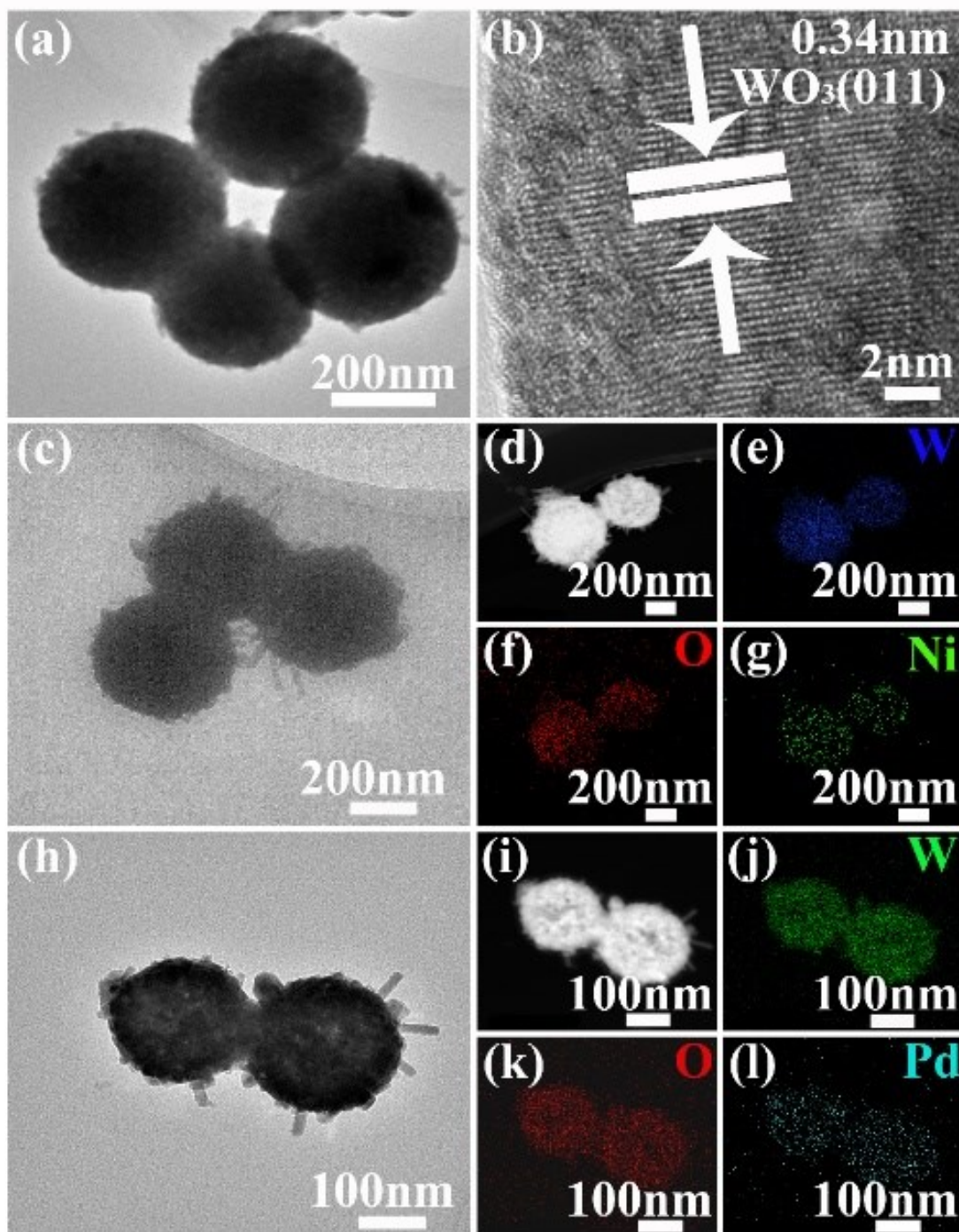


Figure S1 (a, c and h) The transmission electron micrographs of WO_3 , Ni-WO_3 and Pd-WO_3 (b) The HRTEM of WO_3 , (d)-(g) The element distribution of Ni-WO_3 , (i)-(l) The element distribution of Pd-WO_3 .

TEM images of as prepared samples are shown in **Fig S1**. The pure WO_3 nanospheres have a smooth surface (**Fig S1a**) and the diameter between 400 and 500

nm. The Ni-WO₃ nanospheres are given in **Fig S1c**. The surface of the nanospheres is no longer smooth, with diameter ranging from 300 to 500 nm. **Fig S1h** show the TEM image of Pd-WO₃ nanospheres. Pd-WO₃ nanospheres are about 500 nm in diameter. It is obvious that the surface of nanospheres with Ni or Pd is coarser than that of pure WO₃ nanospheres. To achieve more detailed structure information, the HRTEM observations were further employed. **Fig S1d-g** shows the uniformly distribution of W, O, Ni on the surface of Ni-WO₃ nanospheres, respectively. **Fig S1 i-l** shows the uniformly distribution of W, O, Pd on the surface of Pd-WO₃ nanospheres. As shown in **Fig S1b**, the measured d spacings of the nanospheres were 0.34 nm, corresponding to WO₃ (011).

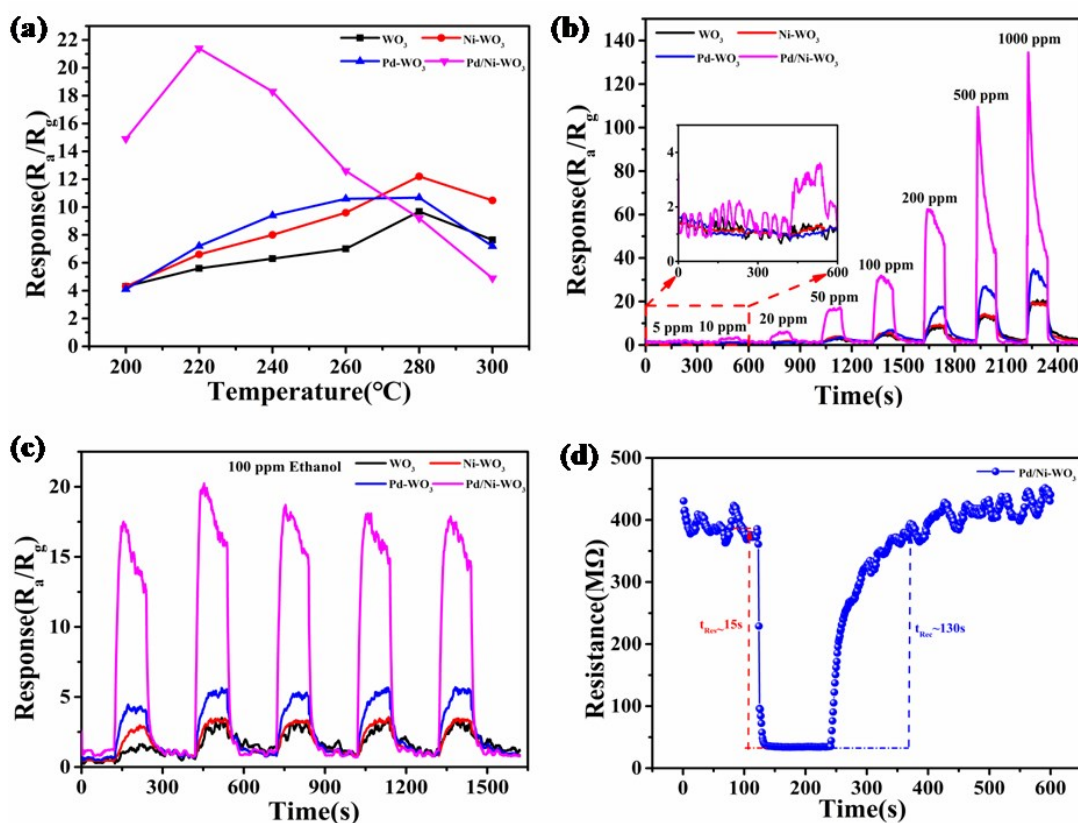


Figure S2 (a) The response of sensors versus operating temperature ranging from 200-300 $^{\circ}\text{C}$ to 100 ppm Ethanol. (b) The change in response of sensors under exposure to

Ethanol with varying concentration from 5-1000 ppm. (c) The repeatability of sensors to 100 ppm Ethanol. (d) The resistance of Pd/Ni-WO₃ devices varies with time to 100 ppm Ethanol.

Firstly, the optimum working temperature of four samples was tested (as shown in **Fig S2a**). As shown in hydrogen, the response of the pristine WO₃, Ni-WO₃, Pd-WO₃ and Pd/Ni-WO₃ samples to 100 ppm Ethanol increased with the increase of temperature, then reached the highest point, and then decreased. At 280°C, WO₃, Ni-WO₃ and Pd-WO₃ nanospheres showed higher response of 9, 12 and 10.5 respectively. The response of Pd/Ni-WO₃ sensor to 100 ppm Ethanol at 220°C can reach 21 compared with bare WO₃, Ni-WO₃, and Pd-WO₃, the optimum operating temperatures of Pd/Ni-WO₃ sensors decreased 70°C. The response-recovery curves of the pristine WO₃, Ni-WO₃, Pd-WO₃, and Pd/Ni-WO₃ to Ethanol with various concentrations at respective optimal operating temperature are also measured (as shown in **Fig S2b**). The Pd/Ni-WO₃ exhibits largest enhancement in the resistance change at lower operating temperature of 220°C, indicating the response of pristine WO₃ to Ethanol has also been significantly improved by bimetallic Pd/Ni decoration. The cycling stability and reproducibility of this sensor was also investigated (as shown in **Fig S2c**). As a result, the Pd/Ni-WO₃ sensor showed an almost identical response towards Ethanol, indicating a good repeatability. As shown in **Fig S2d**, the sensor based on Pd/Ni-WO₃ shows the optimal response and recovery times compare to the other samples. However, it can be clearly seen that the response becomes favorable when WO₃ nanospheres are doped with mono Ni or Pd or double metal. It can be seen that the Pd/Ni-WO₃ exhibit faster response and recovery speeds than other sensors, but to a high concentration of

ethanol gas sensor's response dropped, the detailed mechanism discussed in the gas mechanism section.

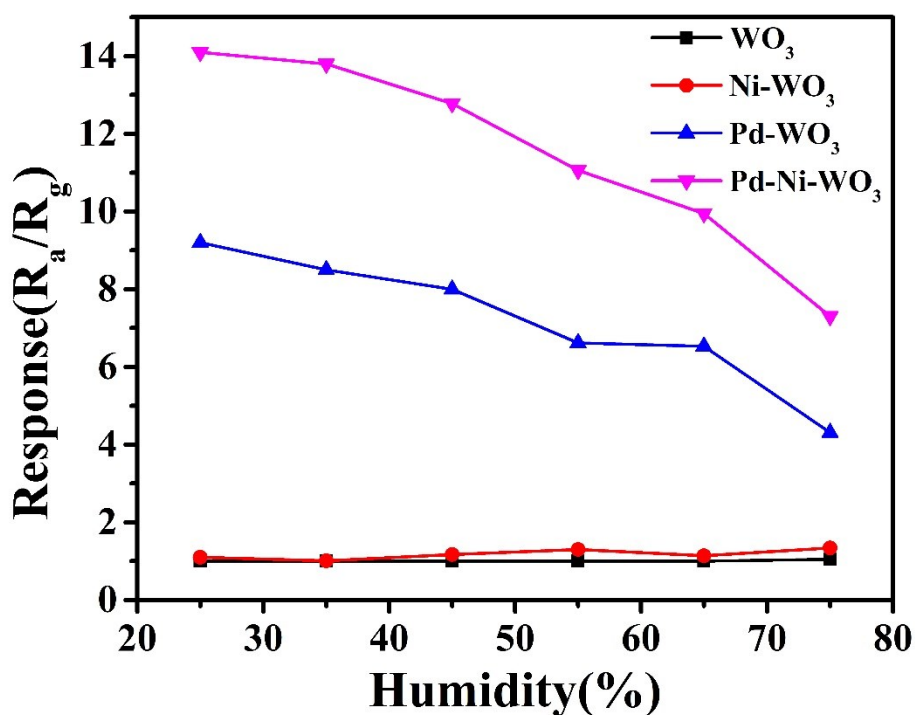


Figure S3 the response of the sensors test in different humidity

Clearly, the sensor response decreased as the relative humidity increased from 25% to 75% as observed in **Fig S3**. Such influence of the water vapor on the response of the metal oxide-based sensors has been reported in literature.

Concentration(ppb)	1	5	10	50	100	500	1000	2000
WO ₃	1.08	1.11	1.44	1.69	1.70	2.24	2.93	3.48
Ni-WO ₃	1.15	1.11	1.18	1.07	1.12	1.09	1.16	1.13
Pd-WO ₃	1.01	1.01	1.03	1.13	1.33	2.72	6.90	18.53
Pd/Ni-WO ₃	1.25	1.43	1.96	2.40	3.45	7.47	14.30	26.64

Table R1 the response value of the sensor to different concentrations of hydrogen

The response value of the sensor to different concentrations of hydrogen is shown in **Table R1**. It is clearly shown that the H₂-sensing response is strongly enhanced by the bimetallic functionalization.