## SUPPORTING INFORMATION

## Two-step exfoliation of WS<sub>2</sub> for NO<sub>2</sub>, H<sub>2</sub> and humidity sensing applications

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**Supporting Figure S1.** Schematic illustration of the exfoliation process. 2 g of WS2 commercial powder with 99% purity and average particle size of 2µm (a) were dispersed in 4 ml of Acetonitrile and ball milled (b) in a planetary milling machine at 400 rpm with with 30g Zirconium Oxide balls (D=3 mm) for 2 hours (steps of 15 min milling and 5 min idle to avoid excessive warming). The ACN residuals were then evaporated overnight (i.e. drying) at room temperature (c). After ACN evaporation, 0.05 g of the ball milled powder dispersed in 100 ml of pure ethanol and probe sonicated (d) for 90 minutes in a cool bath (T 25°C). Finally, the sonicated dispersion was centrifuged at 2500 rpm for 40 min at 20°C (e) and the supernatant collected (f) and spin coated on a proper substrate (g). Some drawings of this figure are distributed by "Servier Medical Art by Servier".



**Supporting Figure S2.** Schematic illustration of the substrate with drop cast exfoliated WS2: (a) Substrate front side showing the deposited area (light grey); (b) SEM picture of the Pt finger-type electrodes on Si3N4 substrate; (c) SEM picture of the 180°C annealed exfoliated WS2; (d) electrical connections to measure the resistance of the WS2 film by volt-amperometric technique.

The electrical resistance of the films was measured by an automated system. Thin film deposited on Si<sub>3</sub>N<sub>4</sub> provided with Pt finger type electrodes was placed inside a Teflon chamber (500 cm<sup>3</sup>), provided with Teflon tubings and exposed to gaseous mixtures containing between 1 ppm to 500 ppm H<sub>2</sub>, between 40 ppb to 10 ppm NO<sub>2</sub> in dry air carrier and air with relative humidity in the range 10-80% Relative Humidity (RH) at 500sccm/min flow rate. The average gas residence time inside the chamber is set at 1 min. Different gas concentrations were obtained by mixing certified H<sub>2</sub> and NO<sub>2</sub> mixtures (500 ppm H<sub>2</sub>, and 10 ppm NO<sub>2</sub> in dry air carrier, by means of an MKS147 multi gas mass controller. Thin film electrical resistance was measured by means of the volt-amperometric technique (AGILENT 34970A) at different OTs in the temperature range 25°C-150°C by heating the Si<sub>3</sub>N<sub>4</sub> substrate through back-side-circuit dc current injections (20–80 mA) as shown in Figure S2. The time scale for gas adsorption and air desorption was fixed at 1 h. Gas response properties have been discussed considering the following features: Base Line Resistance (BLR), i.e. the resistance in dry air at equilibrium; Relative Response (RR), i.e. the ratio (R<sub>G</sub>/R<sub>A</sub>) or (R<sub>A</sub>/R<sub>G</sub>) for a given concentration of oxidizing or reducing gases respectively.



**Supporting Figure S3.** XPS spectra of S 2p core level acquired respectively on (a) pristine WS<sub>2</sub> commercial powder (WS<sub>2</sub> PWD); (b) WS<sub>2</sub> exfoliated by ball milling, drying and sonication at 25 °C

The XPS analysis of the S 2p core level spectra reported in Figure S3 shows the presence of several chemically shifted components, composed of the  $2p_{3/2}$  and  $2p_{1/2}$  doublets. These components are very likely a consequence of the high reactivity and oxidation states number of sulfur. The spectra are characterized by three main components, assigned to WS<sub>2</sub> (component 1, at 162.3 eV), to SO<sub>4</sub> (component 2, at 168.8 eV) and to non-metallic disulfide compounds (S<sub>2</sub>)<sup>2-</sup> (component 3, at 163.7 eV). The presence of SO<sub>4</sub> and (S<sub>2</sub>)<sup>2-</sup> on the surface of the pristine powder is due to air oxidation processes. All the assignments of the S 2p components are in line with literature.[1,2]



**Supporting Figure S4.** Grazing incidence XRD spectra of the as-exfoliated WS<sub>2</sub>; as-exfoliated WS<sub>2</sub> - 200°C annealed for 1 hour. Top right inset shows the close up of the 2 $\theta$  region characteristic of crystalline WO<sub>3</sub>. Peaks of crystalline WO<sub>3</sub>, according to ICDS 98-001-7003, are highlighted by dashed green lines. Notably that after annealing at 500 °C for 1 hour, WO<sub>3</sub> crystalline is formed, whereas the WS<sub>2</sub> peak located at 2 $\theta$  degree 29° disappears.



**Supporting Figure S5.** The electrical response of WS<sub>2</sub> post-annealed at 180 °C at different operating temperatures and 800 ppb NO<sub>2</sub> in dry air. Horizontal black dotted lines mark the base line resistances. NO<sub>2</sub> pulses are represented by the grey shaded rectangular plots. The time scale of the experiment consists of 1 hours conditioning in dry air and 1-hour exposure to NO<sub>2</sub> gases respectively.



**Supporting Figure S6.** Selectivity response of WS<sub>2</sub> post-annealed at 180°C at 150°C operating temperature, respect to 5ppm NO<sub>2</sub>. WS<sub>2</sub> film shows satisfactory selectivity to both 5 ppm H<sub>2</sub> and NH<sub>3</sub> gases and to 250 ppm ethanol and acetone.

## References

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