

Supporting information for:

**Tungsten oxide – lutetium bisphthalocyanine n-p-n hetero-junction: From
nanomaterials to a new transducer for chemosensing**

M. Bouvet,^{a*} M. Mateos,^a A. Wannebroucq,^a E. Navarrete^b and E. Llobet^b

^a *Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), UMR CNRS 6302, Univ. Bourgogne Franche-Comté, 9 avenue
Alain Savary, 21078 Dijon cedex, France. Fax: +33-380-396-098; Tel: +33-380-396-086; E-mail: marcel.bouvet@u-bourgogne.fr*

^b *Microsystem Nanotechnology for Chemical Analysis (MINOS-EMaS), Universitat Rovira i Virgili, Avda. Països Catalans, 26, 43007
Tarragona, Spain. E-mail : eduard.llobet@urv.cat*

Figure S1 corresponds to the ESEM image obtained for a sample of tungsten oxide AA-CVD grown at 370 °C and subsequently annealed at 500 °C for 2 hours in dry air. The sample has been grown onto the application substrate that already comprised interdigitated ITO electrodes. The image shows that the tungsten oxide layer uniformly covers the whole electrode area.

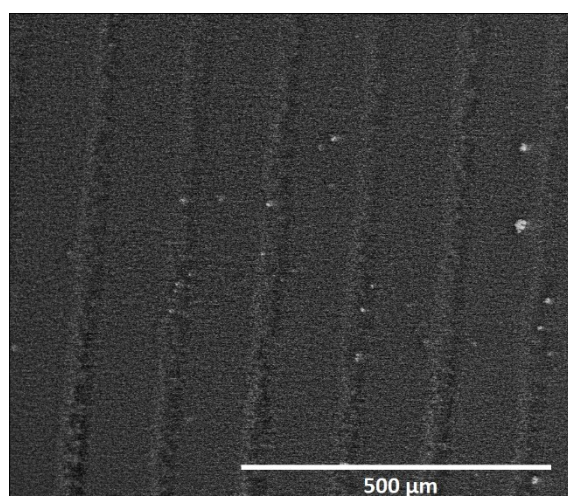


Figure S1. E-SEM micrograph. Interdigitated ITO electrodes are covered with an AA-CVD grown WO_3 layer. The electrode pattern is still visible underneath the 5-micron thick tungsten oxide film.

After the annealing an XRD was carried out to determine the crystalline structure present on the WO_3 film. Figure S2 shows the spectrum obtained. The features in this spectrum match those of the JPDC card 43-1035 for a crystalline tungsten trioxide belonging to the monoclinic system with a space group $P2_1/n$. The cell parameters are $a = 9.05 \text{ \AA}$, $b = 9.07 \text{ \AA}$, $c = 11.61 \text{ \AA}$ and the angle $\beta = 90.77^\circ$. The peaks indicated by an asterisk correspond to the presence of the ITO electrodes on the substrate where tungsten oxide was grown. Once the tungsten oxide film had been coated with the thin Pc_2Lu film, further XRD analysis did not reveal changes to the spectrum shown in Figure S2. This is indicative that the organic film was below 100 nm thick.

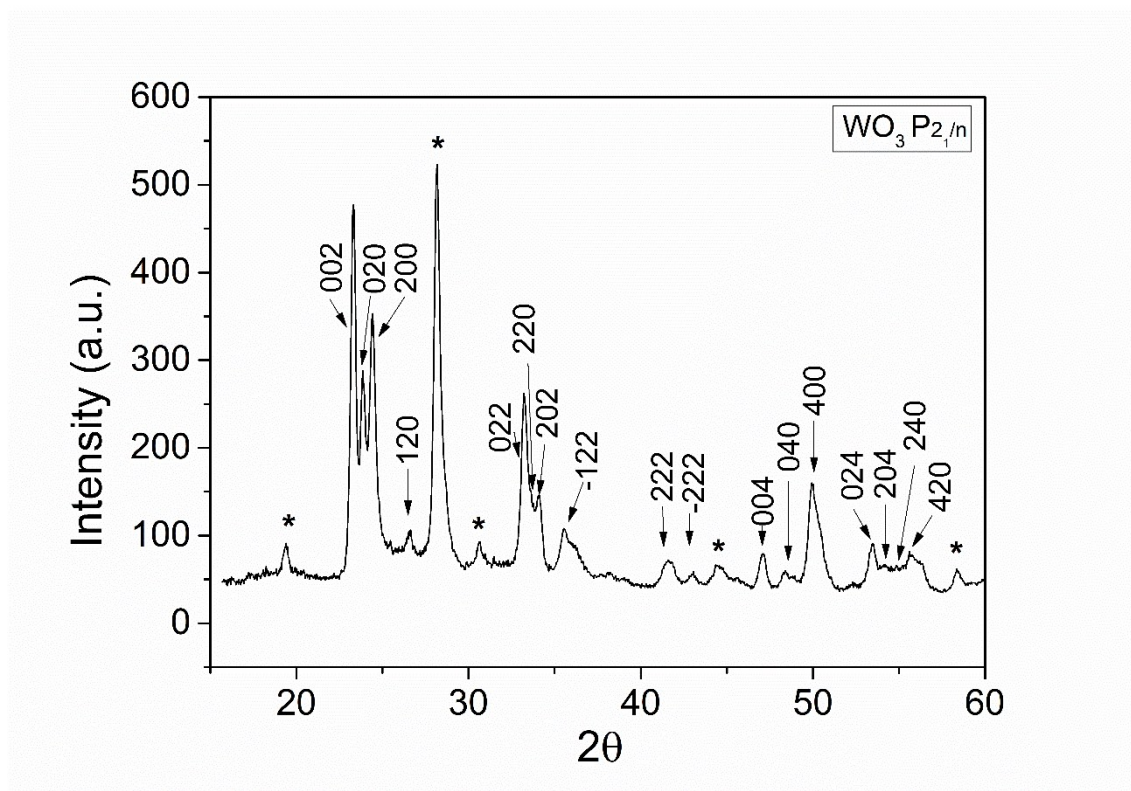


Figure S2. XRD spectrum obtained for the WO_3 nanowire films. Tungsten oxide shows a monoclinic crystalline phase.

Figure S3 shows typical EDX results obtained for an AACVD tungsten oxide film coating a silicate glass substrate in which ITO interdigitated electrodes had been patterned. The Si, Ca and Na peaks correspond to the silicate glass substrate and the In peak can be attributed to the electrodes. The EDX shows clearly the presence of tungsten and, finally, of some carbon contamination, which is often detected in samples exposed to ambient air.

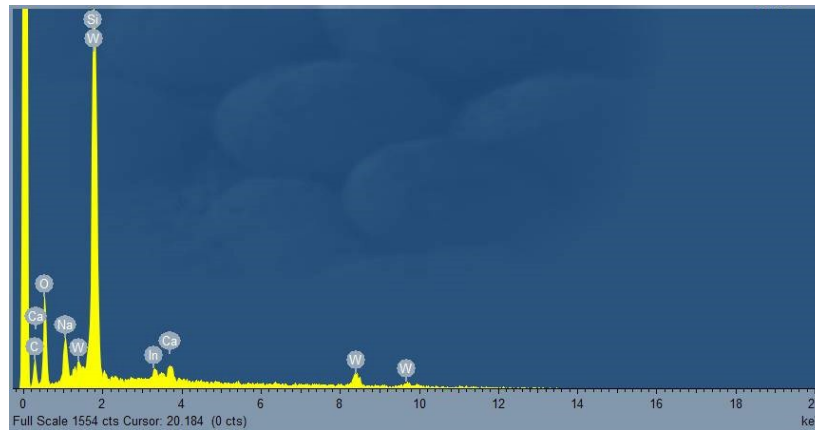


Figure S3. EDX spectrum obtained for an AACVD tungsten oxide film coating a glass substrate having ITO electrodes.

To check the contact between the ITO electrodes and the WO_3 layer a current-voltage curve was measured. A DC voltage sweep was applied to the interdigitated electrodes underneath the tungsten oxide layer. Figure S4 displays these results. The fact that the current-voltage characteristic is almost linear supports the existence of an ohmic contact between the electrodes and the tungsten oxide film.

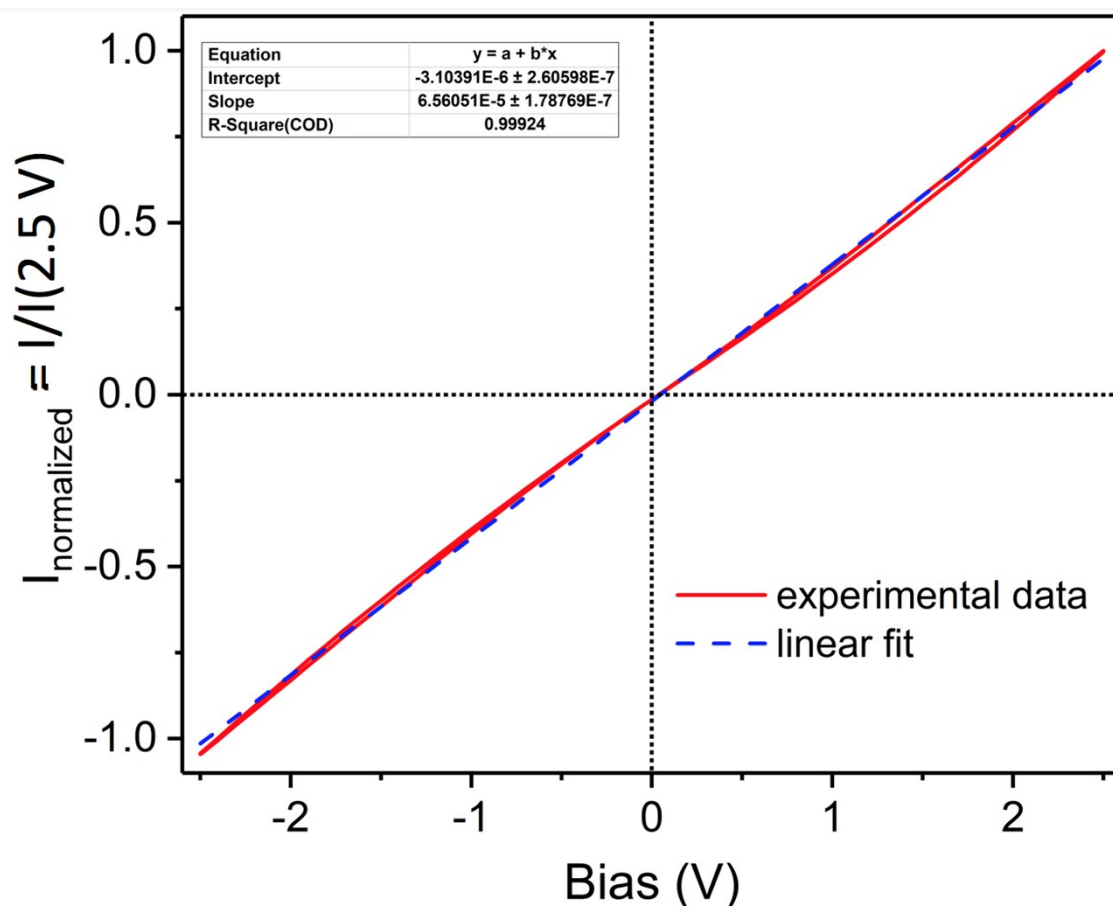


Figure S4. Voltage vs Intensity plot obtained for the WO_3 layer coating interdigitated ITO electrode

To investigate what the limit of detection is for the organic-inorganic MSDI devices discussed here, an experiment was carried out in which low ammonia concentrations were measured repeatedly (1 to 9 ppm). These results are summarized in Figure S5. Response intensity is highly reproducible. The fact that for 1 ppm, the signal is still 6 times higher than the noise level observed, is indicative that the limit of detection for ammonia is clearly below 1 ppm (in the hundreds of ppb range).

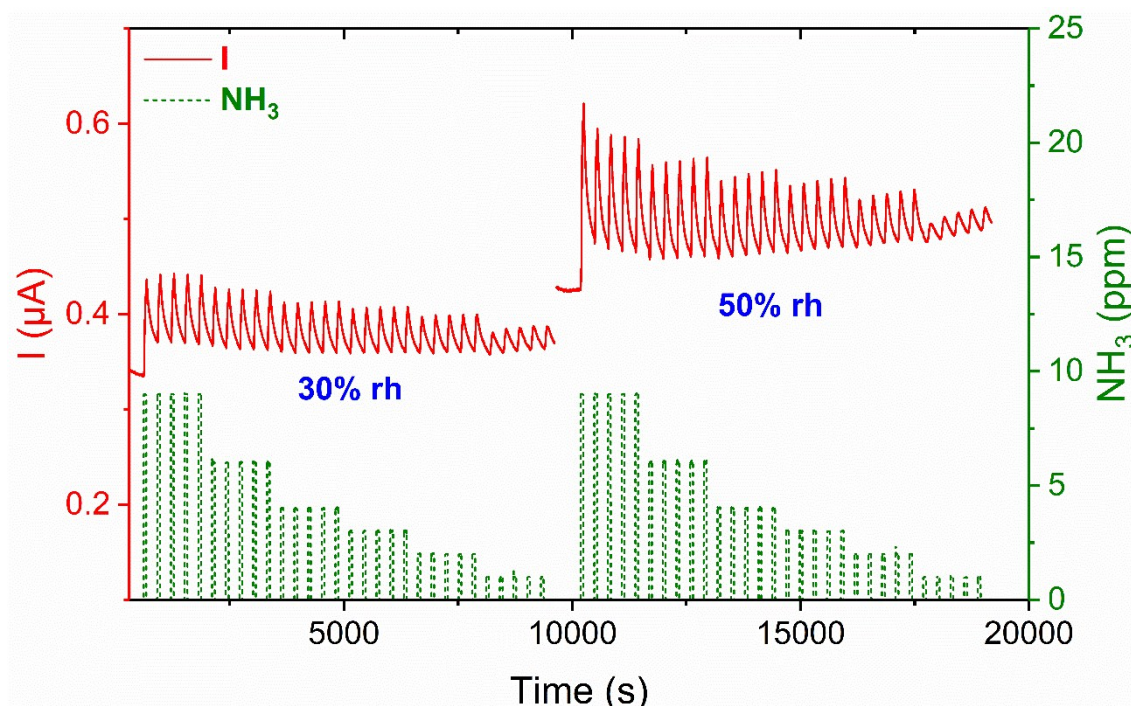


Figure S5. Variation of the current (red line) as a function of time during exposure to NH₃ in the range 1-9 ppm (dotted line), at relative humidity values of 50 % and 30 % (1 min exposure and 4 min recovery); T = 20 °C.