Supporting Information for "Limiting the Oxidation of WS2 Nanostructures by Passivating the Surface Using an Organic Capping Agent for Room Temperature NH_3 Sensing"

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The synthesis of OLA/WS_2 involves the formation of intermediates characterized by colour changes as seen in Figure S1 below. Light yellow OLA (20 mL) was heated and stirred continuously under N_2 gas flow for 15 min in a three-neck round bottom flask at room temperature (Figure S1 (a)). White crystals of $CS(NH_2)_2$ (1.6016 g) were then added to the mixture (Figure S1 (b)) followed by the yellow crystals of H_2WO_4 (1.2492 g) and heated rapidly to 320 °C to allow for the decomposition of both precursors (Figure S1 (c)). The reaction was characterized by several colour changes at different reaction temperatures indicating the formation of intermediates (Figure S1 (k)). The mixture started boiling and turned milky yellow at about 150 °C (Figure S1 (d)); $CS(NH_2)_2$ decomposes between 100 – 120 °C). As the reaction progressed colour changed to grey, green, brown and ultimately thick black (150 – 320 °C, Figure S1 (e – j)) pointing to the formation of WS_2 nanostructures. The colour changes were punctuated by bubbling and foaming followed by smoking and squirting. The oil in the gas bubbler turned yellow (Figure S1, (l)) during the reaction and a white deposit was observed on the joints of the 3-neck round bottom flask (Figure S1 (j)). The reaction was held at 320 °C for 15 min to allow for growth of nanostructures. Subsequent aliquots of the black product were taken at 15, 45, 60, 180 and 240 min. After cooling the samples for 5 min, ethanol was added to separate the colloids from the growth solution. The nanostructures were collected by centrifugation and excess OLA was washed off several times with a 1:1 ratio of ethanol to hexane. The black powders were dried RT and re-dispersed in chloroform for further characterization.

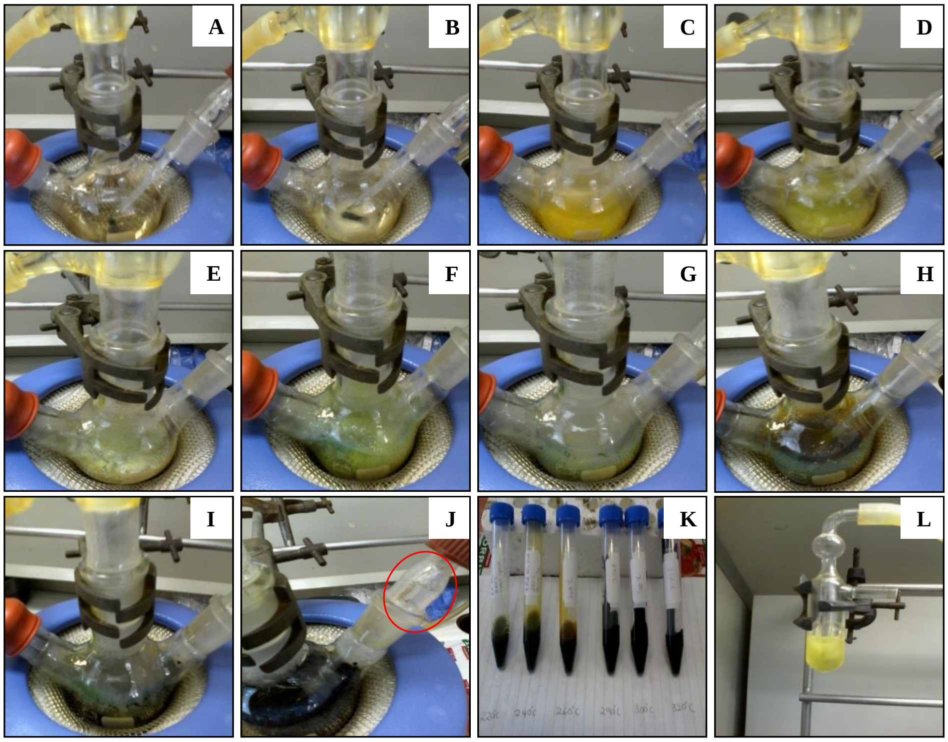

Figure S1. Diagrams showing different colour changes during growth of OLA/WS_2 nanostructures.

EDS analysis confirmed the presence of W and S elements in the samples. All the samples showed the same results, hence only the EDS spectrum for 180 min is presented.

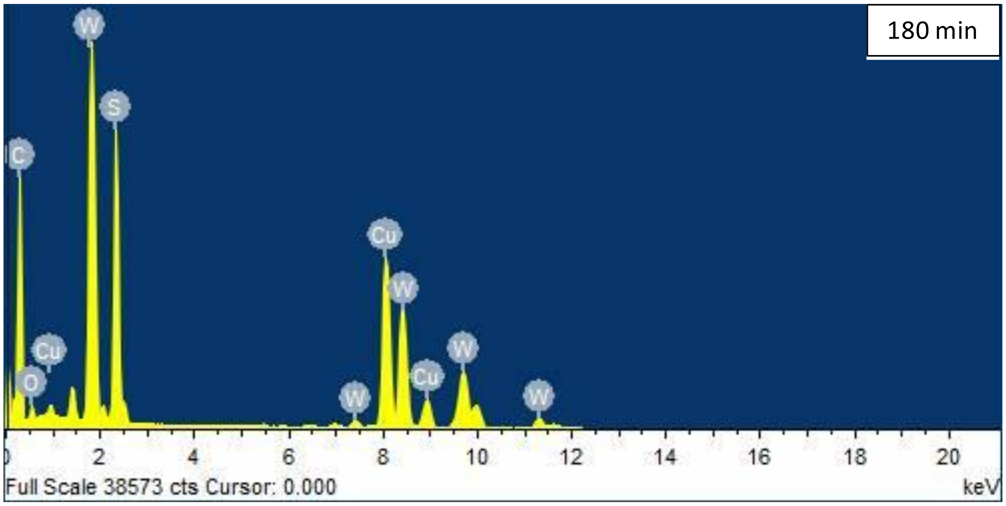

Figure S2. EDS analysis of the 180 min OLA/WS_2 nanostructures.

The frequency difference can also be used as an indication of the number of layers and the values depicted in Table S1 below suggest the formation of bi-layers. The intensities of the 2LA(M) are slightly higher than that of $A_{1g}(\Gamma)$ and the ratios are depicted in Table S1.

Table S1. Raman intensity ratios and frequencies for the main phonon modes in OLA/WS_2.

Sample	**I_{A1g}**	**$I_{2LA(M)}$ (nm)**	**$I_{2LA(M)}/I_{A1g}$**	**Frequency: A_{1g} (cm^{-1})**	**Frequency: 2LA(M) (cm^{-1})**	**$\Delta\omega$ = A_{1g} - 2LA(M)**
15	1.23	1.64	1.33	415	350	65
45	3.30	5.78	1.75	417	351	66
60	3.00	5.27	1.75	416	351	65
180	1.84	2.25	1.22	414	349	65
240	3.00	4.27	1.42	414	349	65

The UV and PL results for all samples are summarized in Table S2.

Table S2. UV and PL Raman intensity ratios and frequencies for the main phonon modes in OLA/WS_2.

Sample	Exciton A (nm)	Exciton B (nm)	Exciton C (nm)	Emission intensity (nm)
15	625	505	430	1727
45	625	505	430	863
60	630	505	440	1181
180	630	515	440	2217
240	630	505	430	402

Figure S3 shows the spectra of pure OLA and OLA/WS_2. All the samples presented the same spectra, hence only the spectra for the 45 min sample is presented. The spectrum of OLA/WS_2 nanostructures resembles that of pure OLA with small shifts in wavenumbers. Compared with the spectrum of pure OLA, the stretching υ(NH) and rocking modes δ(NH) of the amino group at 3320 cm^{-1} and 1571 cm^{-1} respectively are absent for both pure OLA and OLA-WS_2 nanostructures. On the other hand, the υ_{as}(-CH_2) and υ_s(-CH_2) modes of the methylene group for pure OLA are observed at 2916 and 2855 cm^{-1} respectively and corresponded to the OLA-WS_2 peaks found at 2906 and 2839 cm^{-1} respectively. The δ_{as}(-CH_3) and δ_s(-CH_3) modes of the terminal methyl group are observed at 1472 and 1371 cm^{-1} for pure OLA respectively and at 1447 and 1363 cm^{-1} for the nanostructures. The bending (-NH_2) mode is found at 967 cm^{-1} for pure OLA and at 959 cm^{-1} for the nanostructures. The results therefore confirm the capping of the nanostructures by OLA.

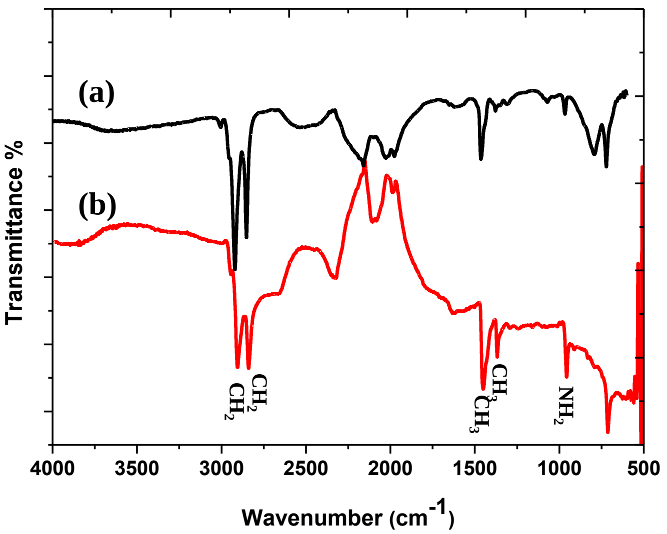

Figure S3. FT-IR spectra of (a) pure OLA and (b) OLA/WS_2 synthesized in 45 min.

The sensitivities for all the samples are summarized in Table S3 below.

Table S3. Sensitivities of OLA/WS_2 based sensors to 1.5 µL of the NH_3.

Sample	**Response**
15	$0.049 \pm 6.6 \times 10^{-4}$
45	$0.047 \pm 1.4 \times 10^{-3}$
60	$0.050 \pm 7.5 \times 10^{-4}$
180	$0.031 \pm 2.5 \times 10^{-3}$
240	$0.018 \pm 1.2 \times 10^{-3}$

The specificity values of the 45 min based sensor are summarized in Table S4 below.

Table S4. Specificity of OLA/WS_2 based sensor (45 min) to 1.5 μL analytes.

Analyte	Concentration (ppm)	Specificity
Acetone	502	0.086
Ammonia	240	0.23
Chloroform	444	0.031
Ethanol	632	0.026
Toluene	352	0.045

Figure S4 shows the dynamic region of the sensor based on the 45 min reaction time for 958 ppm of NH_3. The sensor does not recover to the initial conductance value due to strong interactions between NH_3 molecules and OLA/WS_2 interlayer. However, the device recovered after placing it under UV light for 60 min.