Supporting Information

Direct insight on the confinement effect of WS₂ nanostructures in ordered carbon matrix

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X-Ray Diffraction

Figure SI1 : XRD diagrams of FDU-15/WO_x-350° and FDU-15/WO_x-750° samples. * Symbols indicate the WO_{2.83} related peaks given in the JCPDS database (JCPDS 36-103) up to 65° 2θ.

XPS study

FDU-15/WO_x-750 sample

Figure SI2 : C1s (A), O1s (B), W4f (C) XPS deconvoluted spectra of FDU-15/WO_x-750°.

XPS measurements were done with a VG Scienta SES 2002 spectrometer equipped with a monochromatized AlK_{α} x-ray source (1486.6 eV) and a hemispherical analyzer. The analyzed surface area was 24 mm². The high resolution spectra and wide scan were recorded with pass energy of 100eV and 500eV respectively. The photo-emitted electrons were collected at take-off angle normal from the surface. Peaks were fitted with mixed Gaussian-Lorentzian components using XPS-CASA software, after having subtracted a Shirley-type background. The intensity areas were determined using integrated peak areas of each component and taking into account the transmission factor of spectrometer, mean free path, and sensibility factor of each atom. The spectrometer energy scale was calibrated to the Ag 3d5/2 , core level peaks, set at a binding energy of 386.3 eV.

XPS spectroscopy was used to analyze the surface of the nanocomposites. XPS spectra of FDU-15/ WO_x -750° and FDU-15/ WS_2 -750° samples are presented in SI2 and SI3 respectively. Corresponding data are gathered in Table SI1 and Table SI2. Tungsten peaks position were determined by referring to results obtained on tungsten, particularly WO_x and WS_2 , in literature 27–32.

Table SI1 : Assignment, composition and binding energy of C1s, O1s, and W4f peaks of FDU-15/ WO_x -750°

Block	Assignment	Binding energy (eV)	Composition (atomic %)
C1s	C sp2	284.34	87.18
C1s	C-OR	286.09	0.86
C1s	C=O	287.24	0.59
C1s	COOR	288.44	0.67
C1s	Sat 2	291.54	1.43
C1s	Sat 1	290.04	3.00
C1s	C sp3	285.00	0.00
O1s	<u>O</u>=C-O	531.91	0.67
O1s	O=C-<u>O</u>	533.70	0.67
O1s	H₂O chemisorbed	535.10	0.27
O1s	Sat	537.20	0.08
O1s	C-OR	532.70	0.86
O1s	O=C	531.20	0.60
O1s	W-O	530.40	1.92
W4f	W 4f_{7/2} (W⁶⁺)	35.57	0.64
W4f	W4f_{7/2} (W⁴⁺)	34.20	0.05

FDU-15/WS₂-750° sample

Figure S13: C1s (A), O1s (B), S2p (C), W4f (D) XPS deconvoluted spectra of FDU-15/WS₂-750°.

Firstly, it is important to note that both samples were stored in air with possible oxidation of the W-based phases and of the carbon surface.

For FDU-15/WS₂-750° sample, sulfur is mainly link to carbon and tungsten. W⁴⁺/W⁶⁺ ratio is 6:1 which indicates that WS₂ is largely more present on the surface than WO₃. This ratio probably increases under the surface. The W/C atomic ratio (0.03) is similar to the ratio determined by TG Analysis (0.03).

For FDU-15/WO_x-750° sample, W is present mainly as W⁶⁺ and the W/C atomic ratio (0.007) is lower compared to the sulfide sample (0.03). It suggests that WS₂ structures are more present on the surface than WO_x nanoparticles owing probably to the proposed growth mechanism where W^{x+} diffusion from the carbon wall beneath the surface to the surface where it reacts.

Table SI2 : Assignment, composition and binding energy of C1s, O1s, S2p and W4f peaks of FDU-15/WS₂-750° according to references ²⁷⁻³².

Block	Assignment	Binding energy (eV)	Composition (atomic %)
C1s	C sp²	284.30	59.00
C1s	C-OR	286.05	1.23
C1s	C=O	287.20	0.80
C1s	COOR	288.40	0.89
C1s	Sat²	291.50	1.11
C1s	Sat¹	290.00	2.50
C1s	C sp³	285.00	2.94
C1s	C-S	284.67	6.06
O1s	<u>O</u>=C-O	532.10	0.89
O1s	O=C-<u>O</u>	533.54	0.89
O1s	H₂O chemisorbed	534.93	0.25
O1s	Sat	537.10	0.12
O1s	C-OR	532.63	1.23
O1s	O=C	531.10	0.80
O1s	W-O	530.43	0.94
O1s	S-O	531.55	4.18
S2p	S 2p_{3/2} (WS₂)	162.21	4.29
S2p	S 2p_{3/2} (C-S)	163.70	6.06
S2p	S 2p_{3/2} (SO₃⁻)	168.11	0.70
S2p	S 2p_{3/2} (SO₄²⁻)	168.54	1.80
W4f	W 4f_{7/2} (W⁶⁺)	35.70	0.32
W4f	W 4f_{7/2} (W⁴⁺)	32.62	1.84

Nitrogen adsorption

Figure SI4: Adsorption-desorption isotherms for FDU-15/WS₂ samples.

Table SI3: Results of N₂ physisorption measurements at 77K.

	S_{BET} (m ² .g ⁻¹) *	S_{DFT} (m ² .g ⁻¹) **	$V_{\text{total pores}}$ (cm ³ .g ⁻¹) **	$V_{\text{micropores}}$ (cm ³ .g ⁻¹) **	$V_{\text{mesopores}}$ (cm ³ .g ⁻¹) ***	Mesopores size BJH (nm) ****	Mesopores size DFT (nm) **
FDU-15/ WS₂-350°	163	83	0.29	0.00	0.29	7	7
FDU-15/ WS₂-550°	188	109	0.14	0.04	0.10	5.5	5.5
FDU-15/ WS₂-650°	228	112	0.17	0.04	0.13	6	5.5
FDU-15/ WS₂-750°	279	278	0.19	0.09	0.10	5.5	5.5
C_{worm-like}/ WS₂-750°	320	177	0.21	0.08	0.13	14	16
FDU-15/ WO_x-350°- 0min	82	49	0.16	0.00	0.16	7.5	7
FDU-15/ WO_x-750°	283	327	0.18	0.09	0.09	5	5

* Calculated on the partial pressure domain: 0.067-0.301. It is an arbitrary choice due to the simultaneous presence of micro and mesoporosity. ** Calculated with DFT method and slit pore model. *** Calculated by subtracting the micropore volume from the total pore volume. **** Obtained using BJH method based on Harkins and Jura equation.

For FDU-15/WS₂ samples, N₂ isotherms have all type I and type IV components with high adsorption capacity at low pressure and clear capillary condensation steps around $P/P^\circ = 0.5$ (see Figure SI4). Porous characteristics of these materials are gathered in Table SI3.

A clear increase of the surface area and pore volume, mainly micropore volume, is observed with heat-treatment temperatures in H_2S atmosphere. This phenomenon is usually also encountered in inert atmosphere and is attributed to the generation of micropores due to the formation of volatile species during this carbonization step. Nevertheless, specific surface areas and total pore volume ($V_{\text{total pores}}$) appear relatively low for all samples but this is attributed to the high density of W-loaded carbon materials (see Thermogravimetric Analysis part).

The influence of the sulfidation step on the porosity have been investigated by comparing N_2 sorption results of FDU-15/ WS_2 -750° and FDU-15/ WO_x -750° obtained respectively in H_2S and Ar atmospheres. Interestingly, N_2 sorption results are almost similar (see

Table SI). This suggests that presence of WS_2 rather the WO_x within the carbon matrix do not affect significantly the porosity of the sample since the sulfidation of WO_3 leads to only minor weight and volume variations (+ 7 % and +2 % respectively).

Thermogravimetric analysis

Figure SI5: Thermogravimetric Analysis curves of FDU-15/ WS_2 -750° and FDU-15/ WO_x -750° samples in air atmosphere.

Oxidation of C/ WS_2 composite (FDU-15/ WS_2 -750°) leads to a weight loss in TGA that starts at lower temperature than for C/ WO_x sample. Above 550°, both curves become flat indicating that tungsten-based phase and carbon have been oxidized with only WO_3 remaining as solid phase. At this temperature, weight variation of FDU-15/ WO_x -750° sample is slightly less important than FDU-15/ WS_2 -750° sample. This is due to the difference of behaviors that takes place during the complete oxidation of the W-based phases to WO_3 phase: theoretical

calculations give +1.2 wt% from $\text{WO}_{2.83}$ in FDU-15/ WO_x -750° sample, -6.5% from WS_2 in FDU-15/ WS_2 -750° sample. These analyses give a portion of 37.7 wt % for $\text{WO}_{2.83}$ in FDU-15/ WO_x -750° sample and of 39.5 wt % for WS_2 in FDU-15/ WS_2 -750° sample.