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Supporting information for: Particle size, morphology and phase transitions in hydrothermally produced VO_2(D)

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Further studies were carried out using W-doped VO_2(D) microparticles synthesised using 2-7 at% of WCl_4 (relative to the vanadium precursor) added to the initial solution. The reaction conditions were the same used for the undoped samples Table 1.

Table 1. Sample names and descriptions for VO_2 powders synthesized by the reaction between NH_4VO_3 and $C_2H_2O_4$ in water. NaOH was used to adjust the pH of the starting solution and WCl_4 as the tungsten dopant. All samples were synthesized *via* hydrothermal treatment for 24 hours at 220 °C

Sample	*pH of starting solution*	*Dopant (at %)*
S10	0.96	2
S11	0.93	3
S12	0.99	4
S13	1	5
S14	0.94	6
S15	1	7

W-doped VO_2(D) samples with 2, 3, 4, 5, 6 and 7 at% tungsten were synthesised by addition of WCl_4 to the initial reaction mixture whilst the pH was held constant (pH range 0.9 to 1). Figure 1 shows the XRD patterns obtained from the as-prepared W-doped VO_2(D) samples compared with the VO_2(D) pattern reported in the literature [1]. With ≥ 5 at % additional peaks appear in the pattern, increasing in intensity with increasing W content.

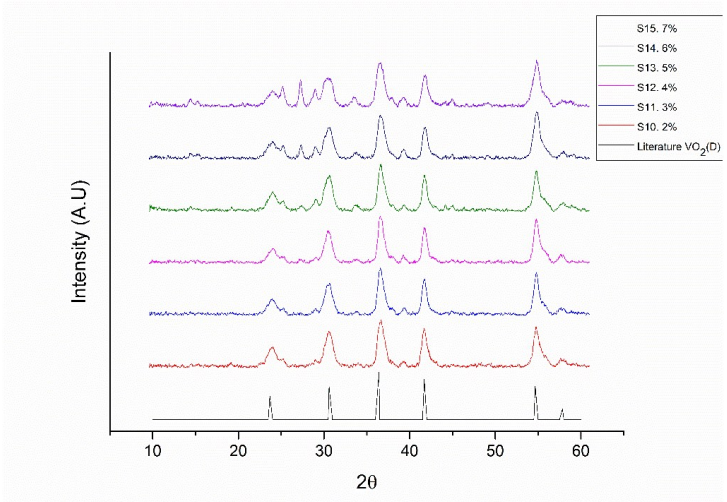

Figure 1. XRD pattern of the obtained VO_2(D) doped with 2, 3, 4, 5, 6 and 7 at% of tungsten compared with the VO_2(D) pattern presented in the literature [1].

These peaks are assigned to WO_3, and suggest the solubility limit of W in VO_2(D) has been reached between at a point below 5% W doping. For sample with less than 5% W doping, the pattern resembles the undoped VO_2(D) pattern, suggesting that low levels of W incorporation into VO_2(D) using this method.

In this experiments, although we can see the presence of tungsten in our samples by EDX (Table 2), XRD analysis shows no change in the VO_2(D) lattice parameters, and at high W doping levels, a secondary WO_3 phase is clearly seen. Additionally, the tungsten does not act as expected to reduce the transition temperature. These results suggest that incorporation of tungsten in this D phase of VO_2 does not occur.

In Table 2 it is shown the information of three of the as prepared doped samples, with 2, 3 and 4% of tungsten (relative to the vanadium amount). The added amounts do not match to the actual amount of tungsten present in the sample, the possible explanation to this is that the tungsten was not incorporated in the lattice of our samples and part of it was washed.

Table 2 Results of added and actual tungsten present in the as-prepared samples

Sample	*Added W-at%*	*Actual W-at%*
S10	2	1.6
S11	3	1.3
S12	4	2.8

The addition of tungsten (different concentrations) to the samples results in a star shape morphology as can be seen in Figure 2 (a-d). In all four cases showed in Figure 2, the stars are composed by rods of around 500 nm, this suggests that the addition of tungsten may retard the particle growth rate.

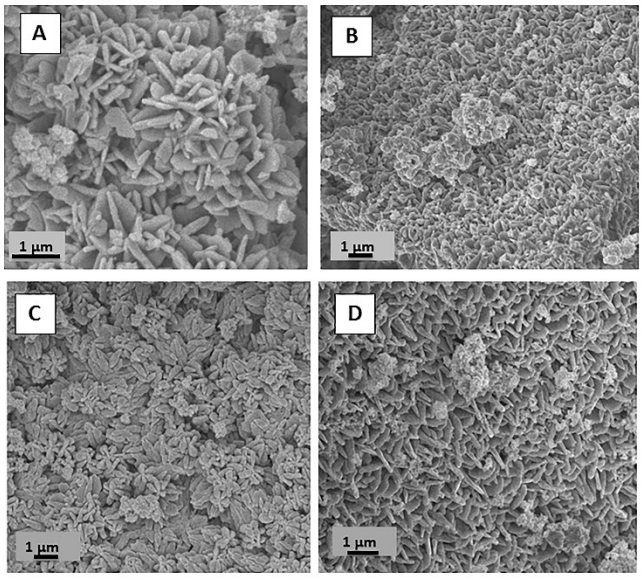

Figure 2 SEM of the W-VO_2(D) prepared samples with (A) 2 at% (B) 3 at% (C) 4 at% (D) 5 at%

The presence of tungsten in the samples seems to suppress the formation of individual spherical particles, instead a mat of elongated particles is formed.

1 L. Liu, F. Cao, T. Yao, Y. Xu, M. Zhou, B. Qu, B. Pan, C. Wu, S. Wei and Y. Xie, *New J. Chem.*, 2012, **36**, 619.