Supplementary Information (SI)

Ammonium hexadeca-oxo-heptavanadate microsquares. A new member in the family of the V_7O_{16} mixed-valence nanostructures

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1. Experimental $KMnO_4$ Permanganometry (Redox Titration)

The permanganometric titration represented by the following equation:

$$5\ VO_2^{+}{}_{(ac)} + MnO_4^{-}{}_{(ac)} + 6\ H_2O_{(l)} \rightarrow 5\ VO_3^{-}{}_{(ac)} + Mn^{2+}{}_{(ac)} + 12H^{+}{}_{(ac)}$$

The permanganometric titration is realized to quantify the proportion of V(V)/ /V (IV) of the oxide state of the mixture. Vanadium (IV) found in the hybrid nanocomposite in both the laminar and micro squares, are inserted in a graph of calibration curve that was made to calculate approximately the V (IV)% in the sample using different concentrations of V (V)/V (IV) with V_2O_5 and V_2O_4 as standard vanadium oxides (Table SI). The preparation mixtures are in a 100 mL Erlenmeyer flask wich 0.100 g of vanadium oxides depending on the different concentrations and dissolved in H_2SO_4 1M at 70 °C over 12h. 25 ml aliquots are taken in triplicate and titrated with 0.1 N $KMnO_4$ 0.1 N standardized previously with $Na_2C_2O_4$.

2. Tables

Table S1. X-Ray photoelectronspectrum (XPS) of $NH_4V_7O_{16}$ nanosquares. Contribution of the components Vanadium (IV) and (V) to the peak V2p3/2. Reference: O1s at 530 Ev

O.E.	Binding Energy (eV)	FHWM (eV)	Area (a.u.)	Area (%)
+4	51588	2,165	37796,8	74,88
+5	517,33	1,725	12677,7	25,12

Table S2. FTIR Spectrum of $(NH_4)_2V_7O_{16}$ microsquares. NH_4^+ ion vibration modes

FT-IR ion NH_4^+ (cm^{-1})			
Assignation	solid	phase gas	
	$(NH_4)_2V_7O_{16}$	$[NH_4(NH_3)_2]$	$[NH_4(H_2O)n]^+$
$\nu_{1\ free}$	3337	2890	3363
$\nu_{3\ free}$	3395 - 3446	3395	3375 - 3365
$\nu_{2\ free}$	1515 - 1556		
$\nu_{4\ free}$	1396 - 1433		
$\nu_{1\ bonding}$	2919	2615 - 2660	2831
$\nu_{3\ bonding}$	3169 - 3198	2865	2961
$\nu_{2\ bonding}$	1691 - 1714		
$\nu_{4\ bonding}$	1617 - 1647	1550 (2 ν_4)	

Table S3. FTIR spectra in the absorption range of oxovanadates for: $(NH_4)_2V_7O_{16}$, the nanocomposite V_2O_5-HDA, VO_xNTs and its precursor[1], and polycrystalline V_2O_5[2,3].

	$\nu_s(VO_A)$	$\nu_a(VO_A)$	$\nu_a(VO_BV)$	$\nu_s(VO_BV)$	$\nu_s(VO_C)$	$\nu_a(VO_C)$	$\delta(VO_{C)}$	$\delta(VO_BV)$
V_2O_5	1023	976	815	472	701	700	502	404
	994			570			510	470
				526			480	
V_2O_5/HDA[1]	956	839			720	640	517	
	911							
V_2O_5/HDA[2,3]	941	854sh			721	646	509	457sh
VO_xNT	997	991sh	797		729		573	
$(NH_4)_2V_7O_{16}$ MC	941				721	644	511	

A: monocoordinated Oxygen, B: bridging oxygen C: three-coordinated oxygen

3. Figures

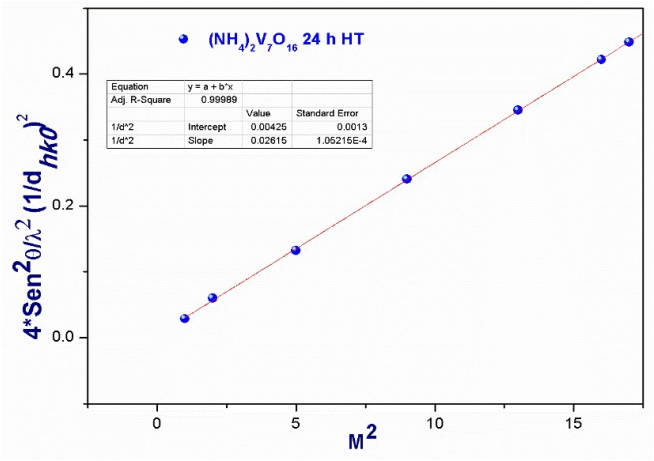

Figure S1. Determination of the two-dimensional cell-constant "a" for $(NH_4)_2V_7O_{16}$, from Bragg (hk0) reflections.

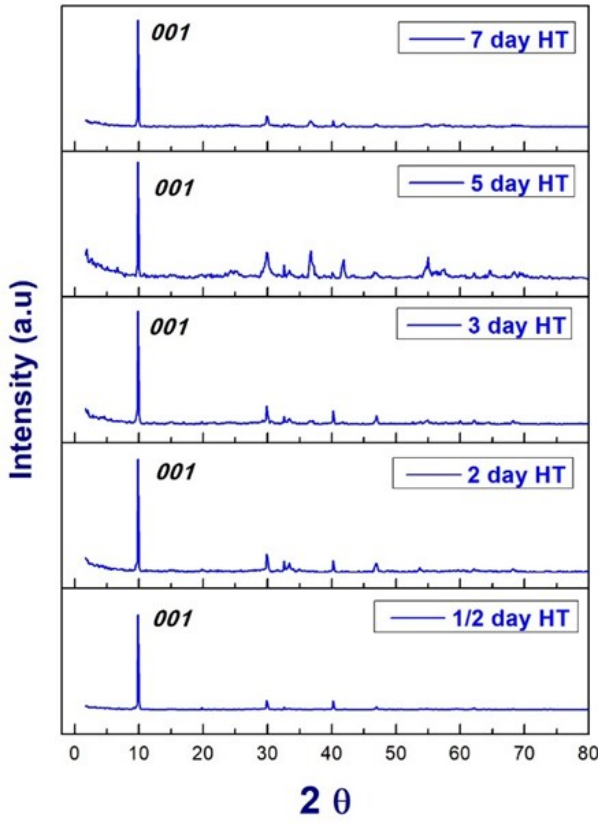

Figure S2. DRX patterns of products prepared with thermal treatments of different duration, from 0.5 to 7 days.

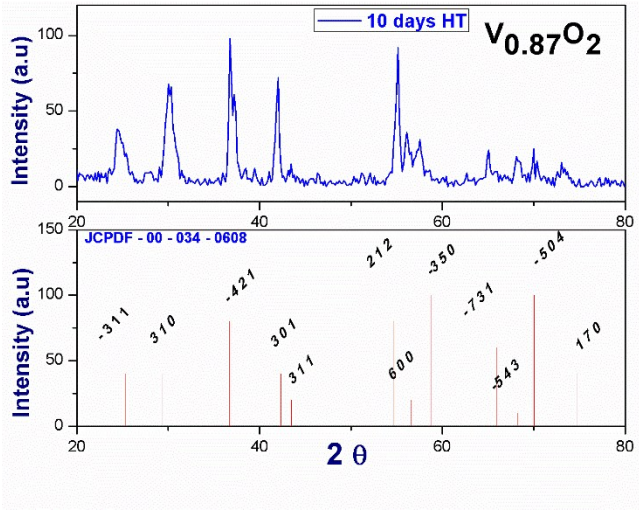

Figure S3. XRD pattern of products obtained after 10 days hydrothermal treatment, compared with the pattern characteristic of VO_2 Magnelli V_xO_2 phases (JCPDS No. 340608).[4]

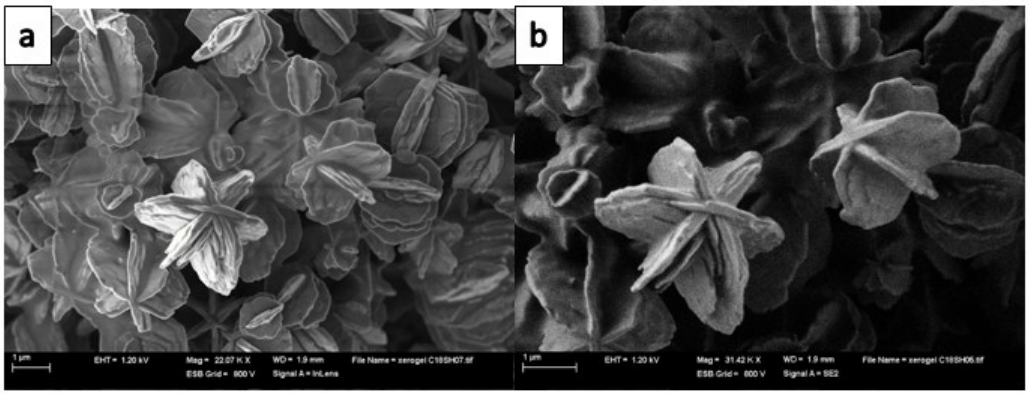

Figure. S4. SEM images of six-times rotationally symmetrical vanadium oxide-based nanostructures with cog-like architecture.[1]

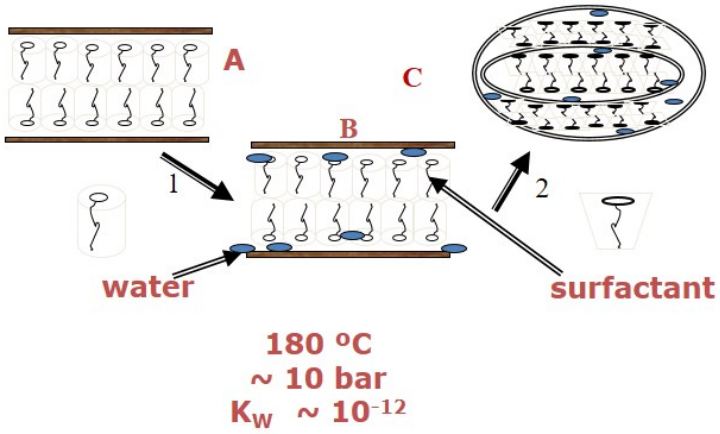

Figure S5. Schematic description of the possible function of alkylamine amphiphiles in the folding and rolling of hybrid sheets V_7O_{16} / amine

Reference

1. W. Chen, L. Q. Mai, J. F. Peng, Q. Xu and Q. Y. Zhu, *J Mater Sci.,* **2004**, 39, 2625–2627.
2. P. Clauws J. Broeckx J. Vennik. *Basic Solid State Phys* **1985**, 131, 459-473
3. L.Abello, E. Husson, R.G. Lucazeau. *Journal of Solid State Chemistry*, **1985**, 56, 379-389
4. C. O'Dwyer, V. Lavayen, D. Fuenzalida, S. Newcomb, M. A. Santa-Ana, E. Benavente and G. González, *Phys. Status Solidi (b),* **2007**, 244, 4157–4160.