Supporting Information

Effect of Surface Properties on the Microstructure, Thermal, and Colloidal Stability of VB_2 Nanoparticles

Bürgehan Terlan[1], Aleksandr A. Levin[2], Felix Börrnert [3,4,5], Frank Simon[6], Martin Oschatz[7], Marcus Schmidt[2], Raul Cardoso-Gil[2], Tommy Lorenz[1], Igor A. Baburin[1], Jan-Ole Joswig[1] and Alexander Eychmüller[1]

[1] Physical Chemistry, TU Dresden, Bergstr. 66b, 01062 Dresden, Germany

[2] Max-Planck-Institute for Chemical Physics of Solids, Nöthnitzer Strasse 40, 01187 Dresden, Germany

[3] IFW Dresden, PF 270116, 01171 Dresden, Germany

[4] Speziallabor Triebenberg, TU Dresden, 01062 Dresden, Germany

[5] Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, United Kingdom

[6]Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069, Dresden, Germany

[7] Department of Inorganic Chemistry, TU Dresden, Bergstr. 66b, 01062 Dresden, Germany

E-mail: buergehan.terlan@chemie.tu-dresden.de

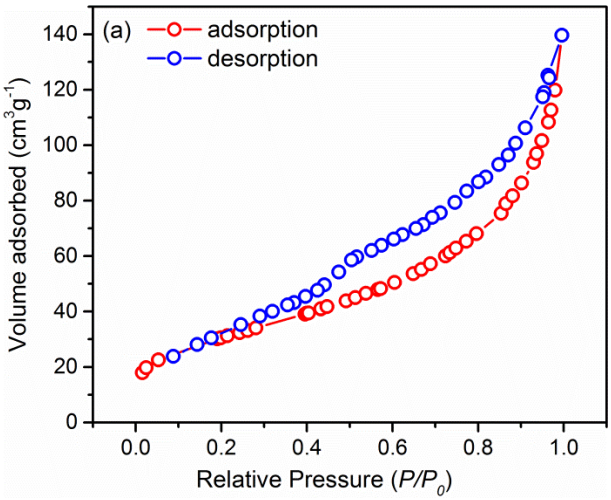
List of Contents

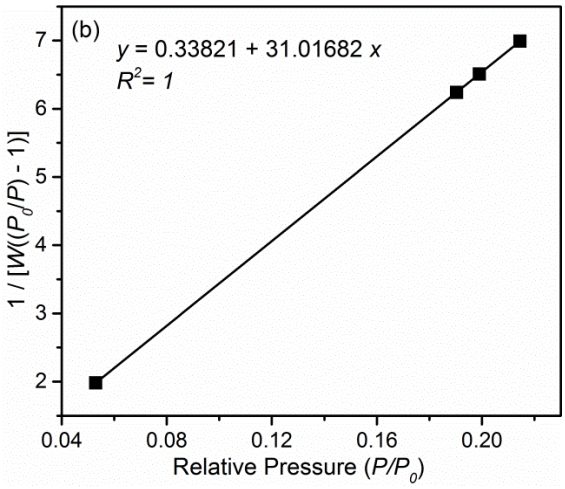
S1 Synthesis: VB_2 nanocrystals were isolated from the eutectic mixture of anhydrous LiCl and NaCl when VCl_3 and $NaBH_4$ were used as starting materials. The possible formation process of VB_2 can be illustrated as follows:

$VCl_3 + 2NaBH_4 \rightarrow VB_2 + 2NaCl + HCl + 7/2H_2$

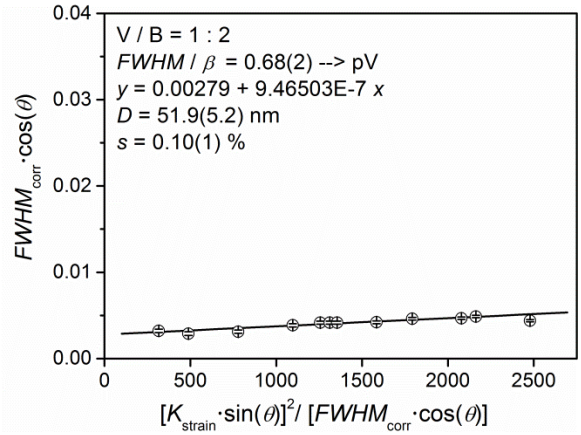
Atomic electron populations based on electron density investigations revealed that B in borane anions is positively charged[73] whereas B in transition metal diborides is negatively charged.[38] On the other hand, V in VCl_3 has an oxidation number of +3 whereas V in VB_2 has an oxidation number of ~ +1. Accordingly, this reaction is a redox reaction where the vanadium atom is reduced by $NaBH_4$.

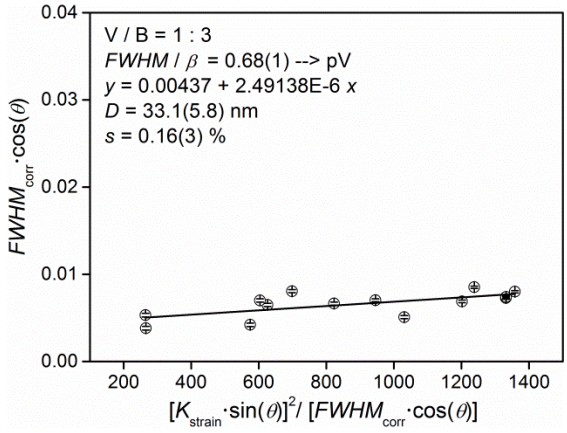
S2 N_2 adsorption-desorption isotherm of VB_2 nanoparticles (initial V / B = 1 : 8) measured at -196 °C (a) and the linear BET plot together with the regression coefficients of the linearly fitted data (b). *W* is the mass of N_2 adsorbed. The BET surface area is 111.1 m^2/g.

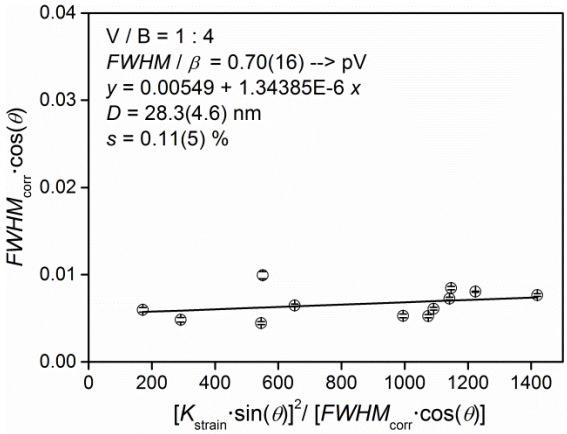


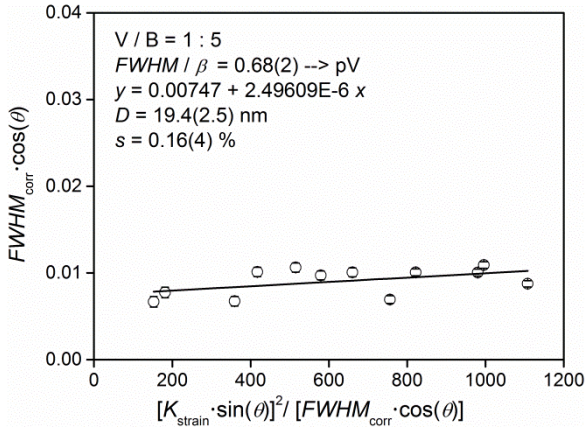


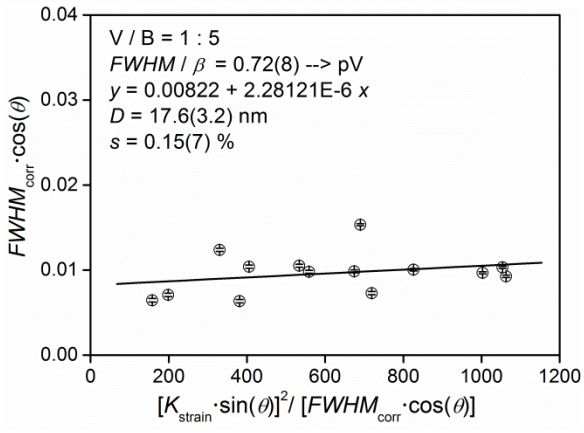
S3 Williamson–Hall plots for VB_2 nanocrystals obtained at 900 °C with varying starting composition (V / B = 1 : 2-8) together with the regression coefficients of linearly fitted data. The form of the X-ray reflection profiles determined according to *FWHM/β* values is pseudo-Voigt. The strain and crystallite size calculated from the slope and *y*-intersect of the respective relationship are also given (K_{strain} = 4).

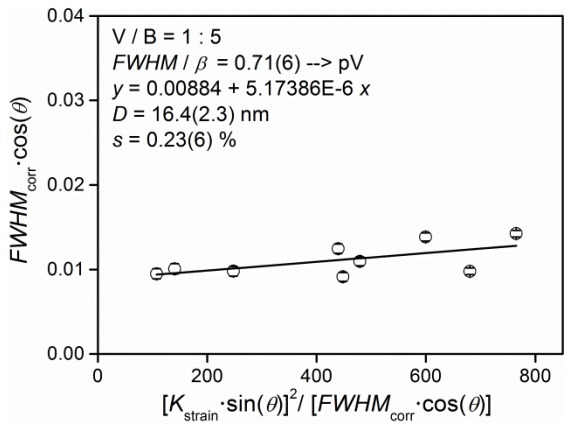


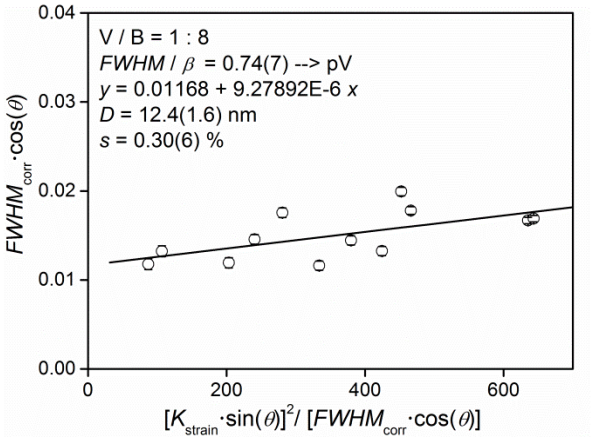


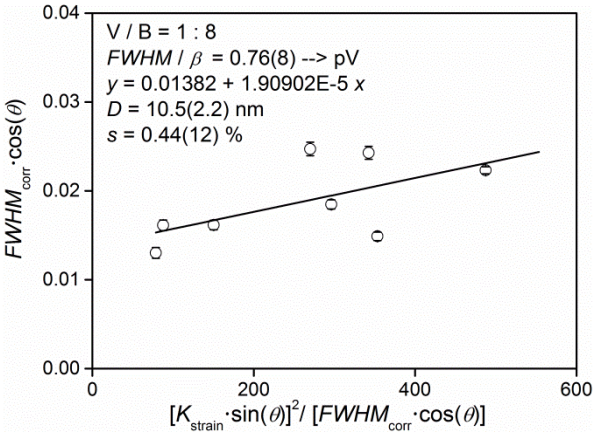


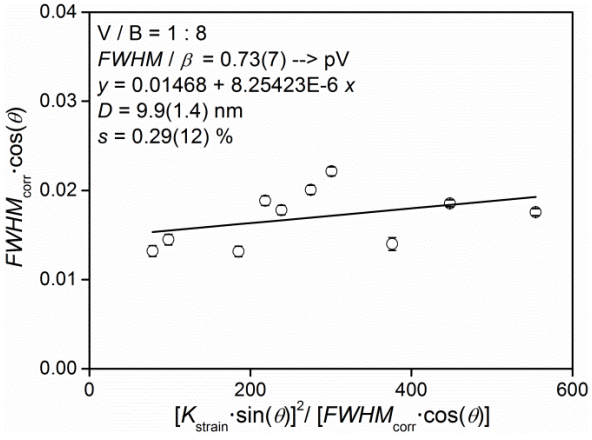




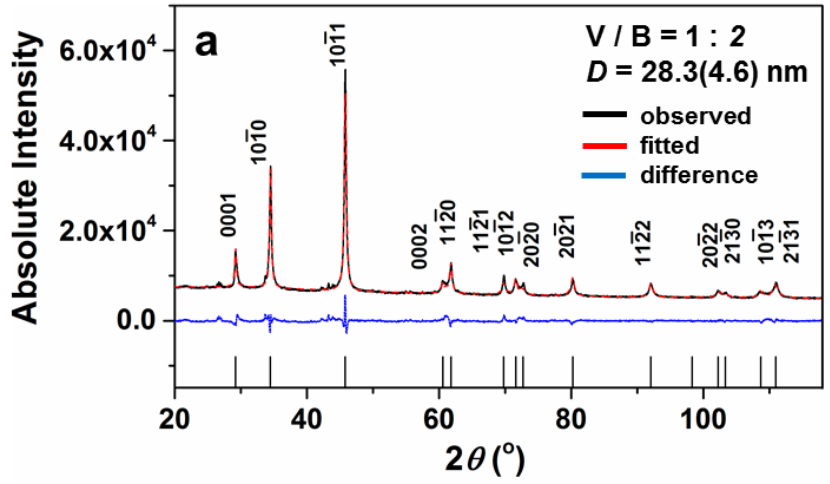



V / B = 1 : 8
FWHM / β = 0.74(7) --> pV
y = 0.01168 + 9.27892E-6 x
D = 12.4(1.6) nm
s = 0.30(6) %
FWHM_corr·cos(θ)
[K_strain·sin(θ)]²/ [FWHM_corr·cos(θ)]

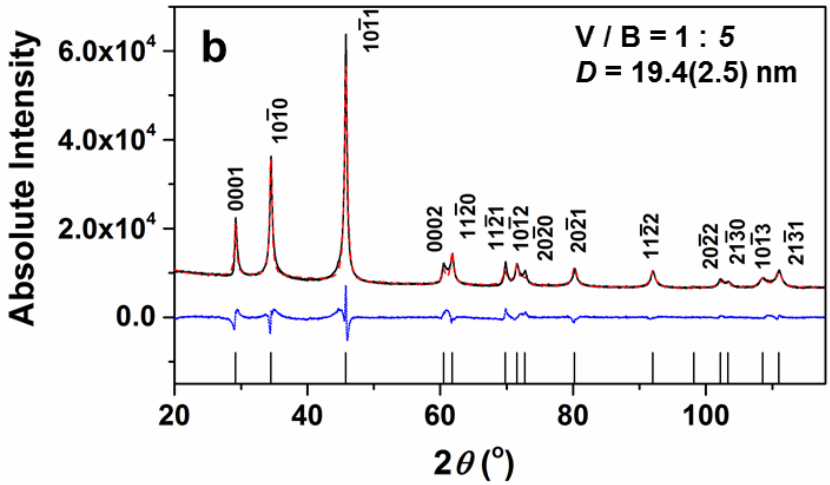

V / B = 1 : 8
FWHM / β = 0.76(8) --> pV
y = 0.01382 + 1.90902E-5 x
D = 10.5(2.2) nm
s = 0.44(12) %
FWHM_corr·cos(θ)
[K_strain·sin(θ)]²/ [FWHM_corr·cos(θ)]


V / B = 1 : 8
FWHM / β = 0.73(7) --> pV
y = 0.01468 + 8.25423E-6 x
D = 9.9(1.4) nm
s = 0.29(12) %
FWHM_corr·cos(θ)
[K_strain·sin(θ)]²/ [FWHM_corr·cos(θ)]

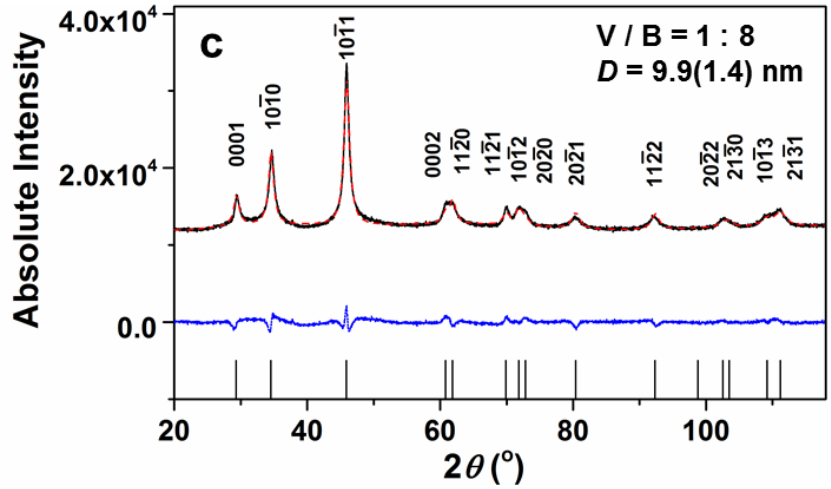
S4 XRD powder patterns of Rietveld refined VB_2 nanocrystals with average crystallite sizes of D = 28.3(4.6) nm (a) D = 19.4(2.5) nm (b) and D = 9.9(1.4) nm (c) prepared with starting composition V / B = 1 : 2, 1 : 5 and 1 : 8, respectively. Black solid line: observed data, red dashed line: fitted curve, blue dotted line: difference between observed data and fitted curve. The vertical lines indicate the 2θ-angle positions of the Bragg reflections. The results of the Rietveld refinement are given in Table.



Unit cell parameters (Å)	a = 3.0005(3) c = 3.0545(6)
V_{cell} (Å^3)	23.8154(67)
R_p (%) / R_{wp} (%)	2.38/3.47
cR_{wp} (%)	15.65
R_B (%)	0.89
$m_{e.s.d.}$	6.05
B_{iso}, V (Å^2)	0.1(1)
B_{iso}, B (Å^2)	0.3(3)
p_{occ}, V	1.001(6)



Unit cell parameters (Å)	a = 3.0000(8) c = 3.0582(14)
V_{cell} (Å^3)	23.836(16)
R_p (%) / R_{wp} (%)	2.87/4.53
cR_{wp} (%)	19.09
R_B (%)	0.93
$m_{e.s.d.}$	7.57
B_{iso}, V (Å^2)	0.1(1)
B_{iso}, B (Å^2)	0.3(3)
p_{occ}, V	0.984(60)

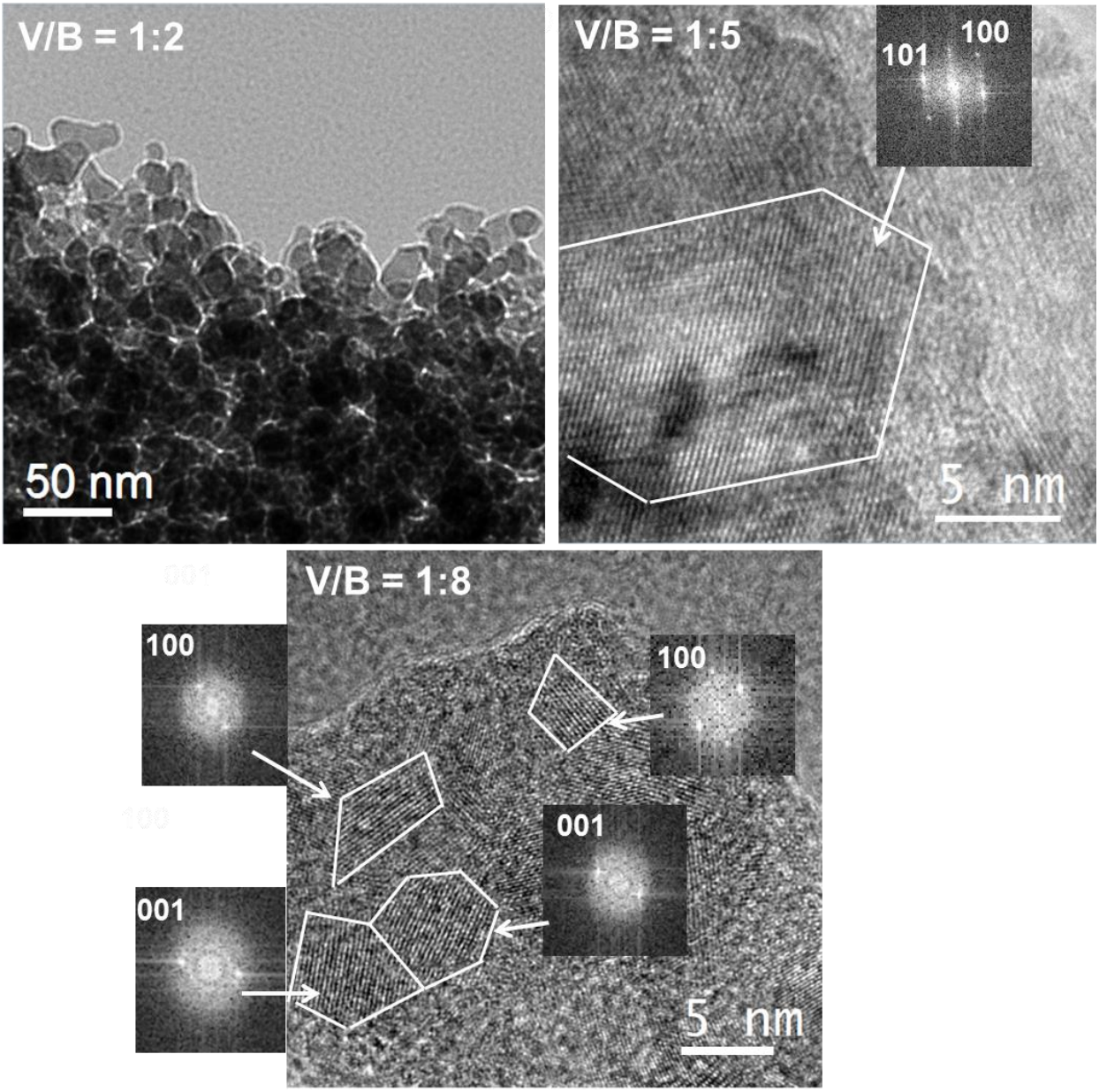


Unit cell parameters (Å)	a = 2.9973(13) c = 3.0447(21)
V_{cell} (Å^3)	23.689(26)
R_p (%) / R_{wp} (%)	1.41/1.89
cR_{wp} (%)	15.68
R_B (%)	0.42
$m_{e.s.d.}$	
B_{iso}, V (Å^2)	0.1(1)
B_{iso}, B (Å^2)	0.3(3)
p_{occ}, V	0.999(71)

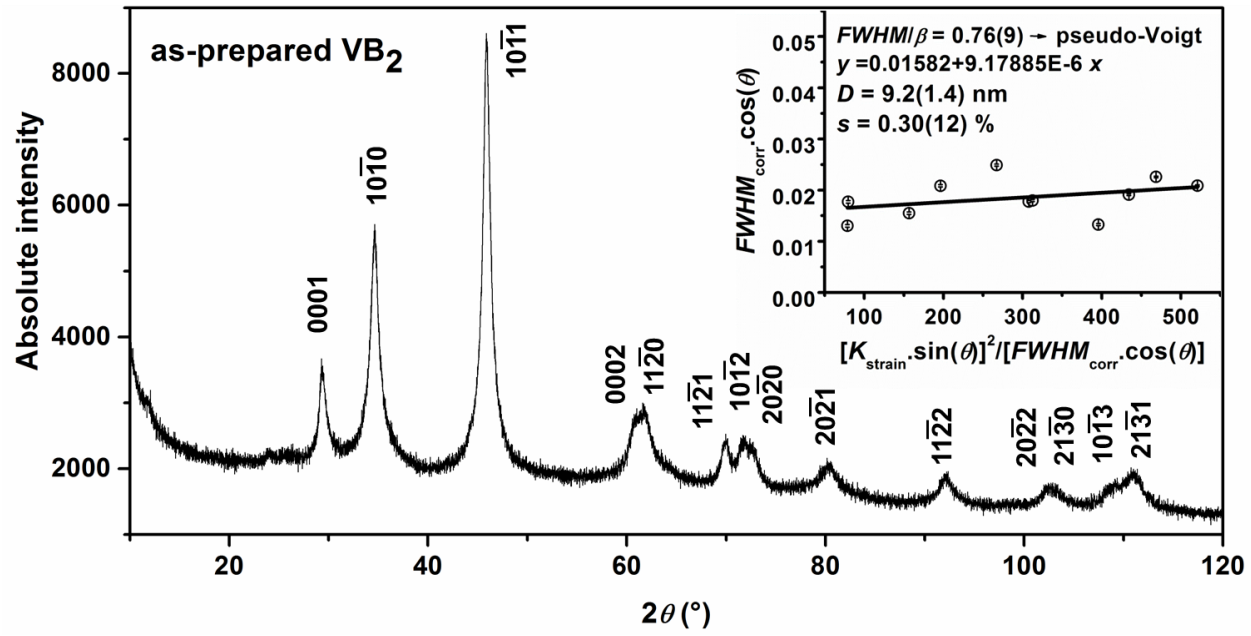
Rietveld refinement protocol

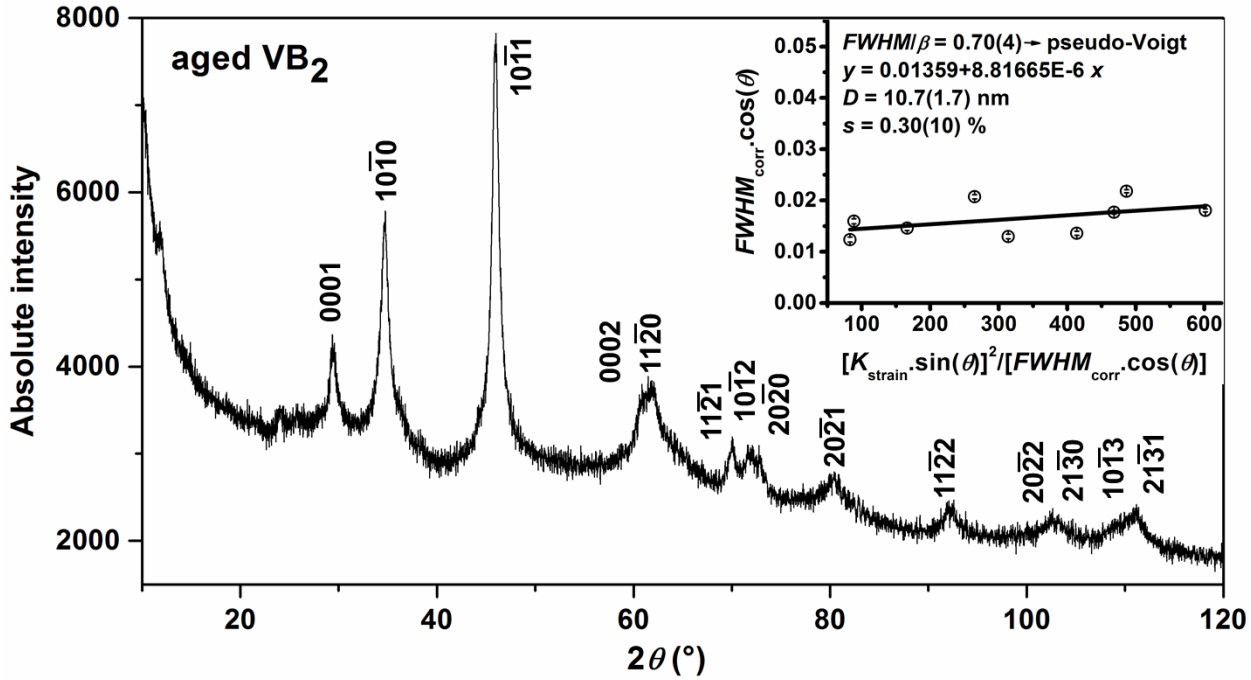
The Rietveld fitting of the XRD powder patterns of VB_2, is performed using the program TOPAS[74] applying the weighting scheme $w_i = 1/y_i$ where y_i is the recorded intensity at step i. The background is fitted by means of Chebyshev polynomial. In the VB_2 structure (space group $P6/mmm$) the V atom is placed at 1a Wyckoff position (relative coordinates x, y, z = 0, 0, 0) with site symmetry 6/mmm, whereas B atom is placed at 2d Wyckoff position (relative coordinates x, y, z = 1/3, 2/3, 1/2) with site symmetry $\bar{6}m2$. Number of formula units, Z is 1. For all refinements, the isotropic description of the atomic displacement was used for both atoms. The refinement of the occupancies of V atom positions did not indicate any deviation from the exact stoichiometry for all three samples. The estimated standard deviations (*e.s.d.s*) of the refined structural parameters (*e.g.* unit cell parameters, B_{iso}, p_{occ}, *etc*.) which were underestimated in the Rietveld refinement due to serial correlations, were corrected by multiplication on Berrar's formalism by means of program *Riet_esd*[75]. In the Table, the obtained values of the structure parameters (unit cell parameters a and c and unit cell volume V_{cell}, B_{iso}, p_{occ}), XRD pattern fitting quality characteristics (profile factor R_p, weighted profile factor R_{wp}, corrected to background weighted profile factor cR_{wp}), structure agreement Bragg factor R_B and Berrar's correcting coefficient $m_{e.s.d.}$ are presented.

S5 TEM micrographs of VB_2 nanoparticles with varying starting compositions (V / B = 1 : 2, 1 : 5 and 1 : 8). The nanoparticles are embedded in an amorphous matrix. Corresponding SAED pattern of VB_2 nanocrystals obtained with V / B = 1 : 8 is shown in the inset.

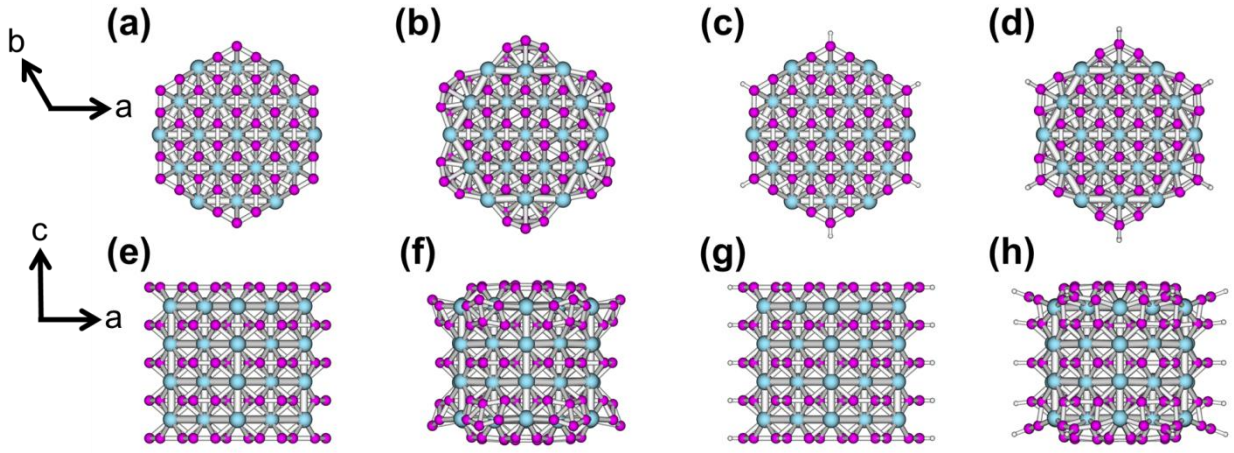


S6 XRD powder patterns of as-synthesized VB_2 nanocrystals (initial V / B = 1 : 8) and those exposed to highly humid environment (aged) for one week. The Williamson-Hall plots for VB_2 together with the regression coefficients of linearly fitted data are shown in the inset. The form of the X-ray reflection profiles determined according to *FWHM/β* values is pseudo-Voigt. The crystallite size *D* and lattice strain *s* values calculated from *y*-intersect and the slope and of the respective relationship are also given (K_{strain} = 4). Please note that the crystallite size and lattice strain values do not indicate a significant difference between the as-synthesized and aged VB_2.





S7 Structural views of a VB_2 nanoparticle along *c*-axis (a-d) and *b*-axis (e-f) without (a, b, e, f) and with (c, d, g, h) hydrogen-saturated edges. Snapshots (a), (c), (e), and (g) show the initial structures used for the geometry optimization and the calculation of the energy as a function of contraction / elongation, snapshots (b), (d), (f), and (h) show the structures of the optimized particles. The vanadium, boron and hydrogen atoms are drawn as blue, purple and white spheres, respectively.



S8 Interatomic distances in the first coordination sphere in the VB_2 nanoparticle with and without H-saturated edges. The values are averages over all distances of the respective type in one particle. Variations with respect to the distance in the optimized VB_2 bulk structure are given in percent.

	Bulk	**NP no saturation**		**NP H edge**	
Ratio V : B	1 : 2	1 : 2.76		1 : 2.76	
V-V (*ab*)	2.954 Å	2.878 Å	-2.57%	2.900 Å	-1.84%
V-V (*c*)	2.921 Å	2.918 Å	-0.11%	2.872 Å	-1.69%
B-B (*ab*)	1.706 Å	1.790 Å	4.91%	1.753 Å	2.74%
B-B (*c*)	2.921 Å	2.679 Å	-8.29%	2.722 Å	-6.82%
V-B	2.246 Å	2.230 Å	-0.69%	2.213 Å	-1.45%

S9 Additional References

(73) Bader, R. F. W.; Legare, D. A. Properties of atoms in molecules: structures and reactivities of boranes and carboranes. *Can. J. Chem.* **1992**, *70***,** 657-676.
(74) *DIFFRAC*^{plus} TOPAS, Version 4.2, Bruker AXS GmbH, Karlsruhe, 2009.
(75) Levin, A. A.; Filatov, S. K.; Paufler, P.; Bubnova, R. S.; Krzhizhanovskaya, M.; Meyer, D. C. Temperature-dependent evolution of $RbBSi_2O_6$ glass into crystalline Rb-boroleucite according to X-ray diffraction data. *Z. Kristallogr*. **2013**, *228*, 259-270.