Electronic Supplementary Material (ESI) for Nanoscale.

A Colloidal Route to Semiconducting Tungsten Disulfide Nanosheets with Monolayer Thickness – Supporting Information

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Preliminary data on WS_2 synthesis

The factor ranges used in the DSD design are based on previous experimental work. To find a suitable range of values, we construct a DSD table and we then proceed to run the synthesis with the lowest factor values combination, since we hypothesize it would be the reaction that would most likely fail (*i.e.* resulting in the lack of measurable responses for the DSD framework). In **Figure S1** we report the UV-Vis absorption spectra of the preliminary data while in **Table S1** we report the factor values used in the synthesis.

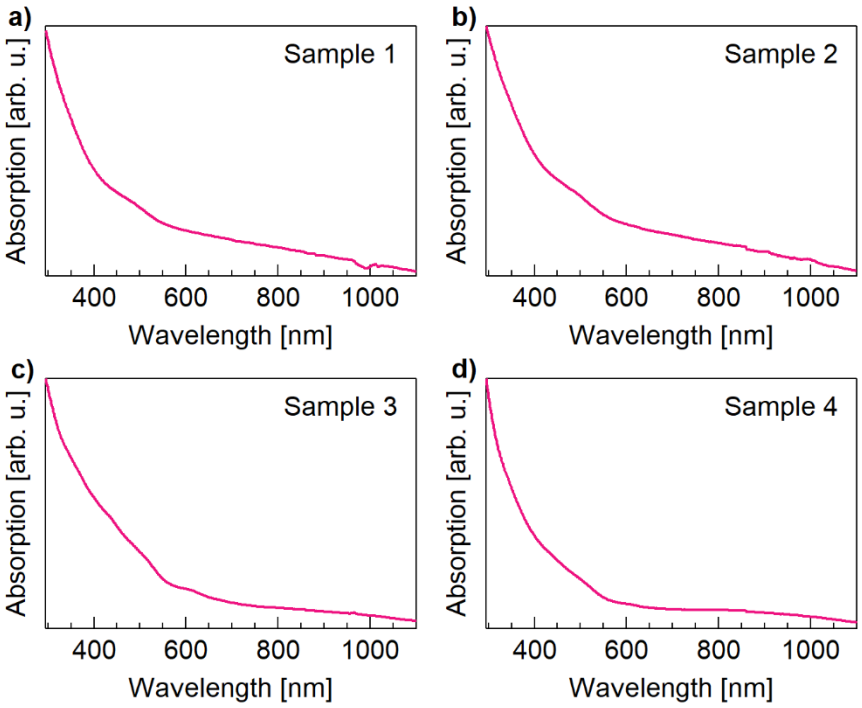
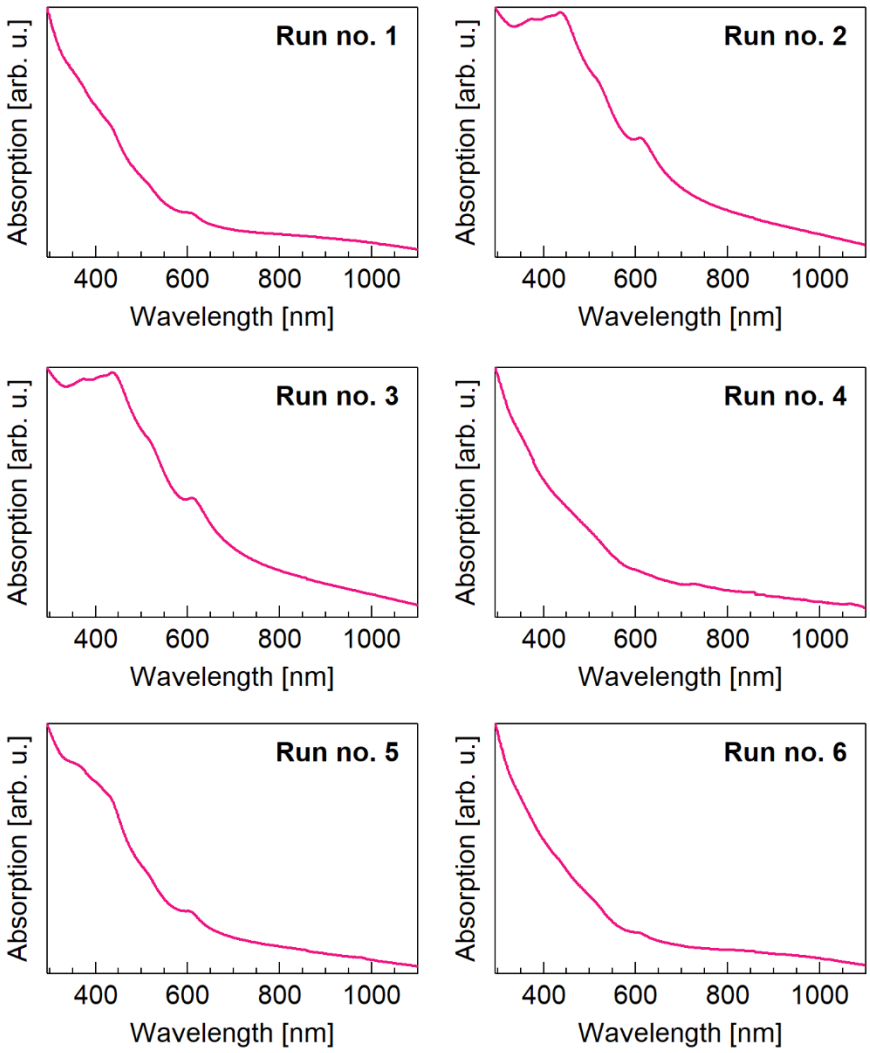


Figure S1. Absorption spectra of sample 1 (a), sample 2 (b), sample 3 (c), and sample 4 (d) used to determine the factor ranges in the DSD framework.

Table S1. Input factor Xi (i = [1, 4]) used in the preliminary experiments. X_1 = Reaction temperature, X_2 = Injection rate, X_3 = S/W molecular ratio, and X_4 = OA/W molecular ratio.

Sample no.	X_1 [°C]	X_2 [mL h^{-1}]	X_3	X_4	HMDS/W ratio
1	300	12	2	2	2
2	310	12	2	2	2
3	310	2	8	30	20
4	310	8	4	10	20



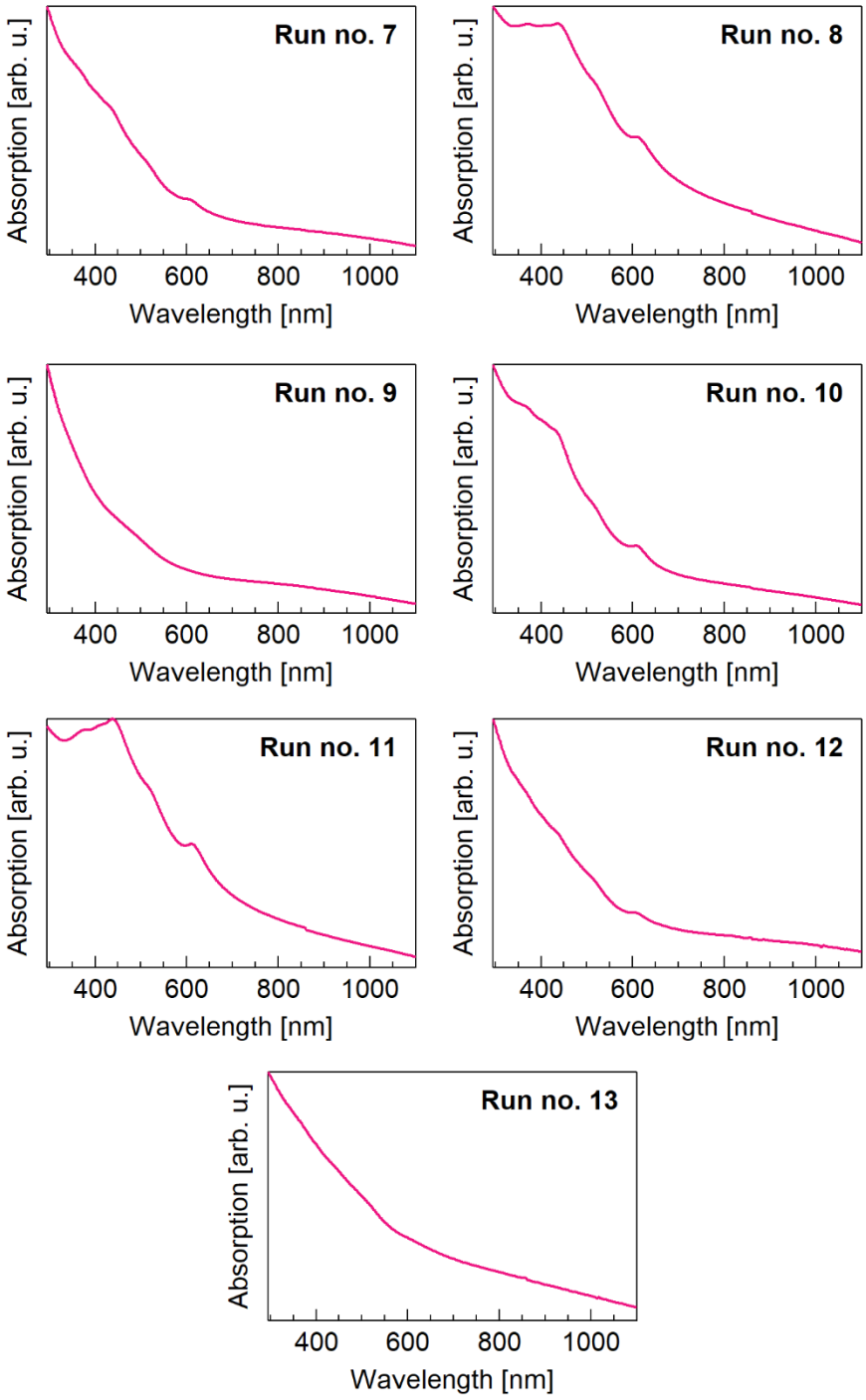


Figure S2. UV-Vis spectra of all the samples used in the DSD design.

Design of Experiments – Definitive Screening Design on WS_2

General note. In the DSD model, each response *Yi* is fitted using a quadratic surface that involves linear as well as quadratic interactions between the input factors X_i, X_i^2, and $X_i \cdot X_j$. In order to avoid model overfitting, we decided to minimize the Bayesian Information Criterion (BIC),[1] keeping at the same time a low corrected Akaike Information Criterion (AICc).[2] See references for further details.

A exciton sharpness. For the modelling, run no. 12 is discarded as it is identified as outlier. Such choice is made after correlating the residuals (calculated as the difference between the measured value and the predicted value) with the values of A exciton position predicted by the DSD model. Run no. 12 displays the highest residual among all runs (**Figure S3a**). A further check has been done using the studentized residuals (**Figure S3b**), calculated by dividing the residual by an estimate of its standard deviation; the standard deviation for each residual computed with the observation excluded. Such studentized value indicates how far (in standard deviation units) the single value (in this case the A exciton position) is from the average error. A value falling in the region delimitated by the red lines (where the standard deviation distance from the average error is 4) is considerate an outlier. Thus, run no. 12 A exciton value falls in the outlier region, and we excluded from the model.

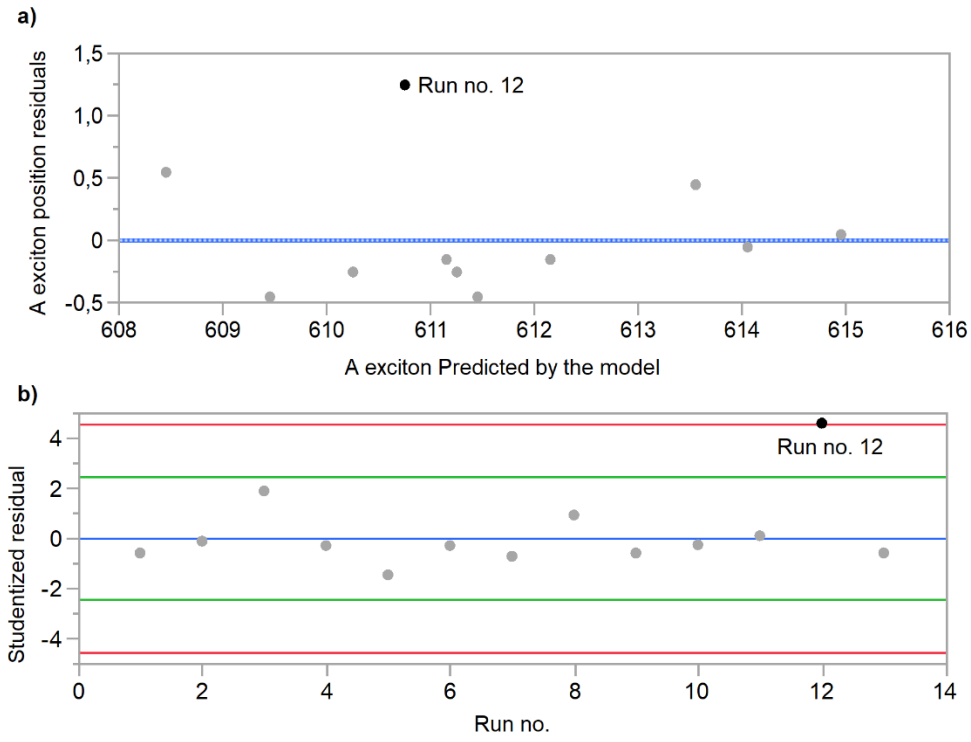


Figure S3. a) Correlation between the experimental residuals of the of A exciton position versus the values of A exciton position predicted by the DSD model. The blue line indicates a perfect match between experimental and predicted values, the dots represent each run result. b) Studentized residuals associated to each run. The red lines indicates the border region where a value is considered an outlier.

The model consists in a total of six factors, consisting in three main factors (injection rate, reaction temperature and S/W ratio), one two-factors interaction (reaction temperature · injection rate), and two quadratic interactions (reaction temperature · reaction temperature and S/W ratio · S/W ratio). The associated *p*-values are reported in **Table S2**.

Table S2. Factors interactions and relative *p-values* for A exciton sharpness model.

Factors		*p*-values
X_2	Injection rate	0.00010
X_1	Reaction temperature	0.00083
$X_1 \cdot X_2$	Reaction temperature · Injection rate	0.00172
X_3	S/W ratio	0.00210
$X_1 \cdot X_1$	Reaction T · Reaction T	0.03209
$X_3 \cdot X_3$	S/W · S/W	0.03560

Background scattering. For this analysis all runs are considered. We found a total of seven factors, featuring four main factor interactions (injection rate, reaction temperature, OA/W, S/W), two two-factor interaction (reaction temperature · OA/W and OA/W · S/W), and one quadratic interaction (OA/W · OA/W). The associated *p*-values are reported in **Table S3**.

Table S3. Factors interactions and relative *p*-value for background scattering model.

Factors		*p*-values
X_2	Injection rate	0.00002
X_1	Reaction temperature	0.00006
X_4	OA/W ratio	0.00015
X_3	S/W ratio	0.00027
$X_4 \cdot X_4$	OA/W · OA/W	0.00367
$X_1 \cdot X_4$	Reaction T · OA/W	0.00473
$X_4 \cdot X_3$	OA/W · S/W	0.01122

Nanosheet size- comparison between optimized samples and run no.11.

In **Figure S4** we report the HR-TEM images of A exciton, background optimized and the bright-field TEM images of run no. 11. Panels a-c are display the HR-TEM of the A exciton optimized sample, while panels d-f display the HR-TEM images of the background optimized sample. both samples show similar nanosheet morphology, with the visible edges of the nanosheet having an average length of 17 nm and standard deviation of 8 nm for the A exciton optimized sample and an average length of 16 nm and standard deviation of 7 nm for the background optimized sample. A comparison with run no. 11 sample (which displays a red shifted exciton position compared to the optimized samples, panels g-i) reveal nanoflower morphology and a larger average size (~50 nm).

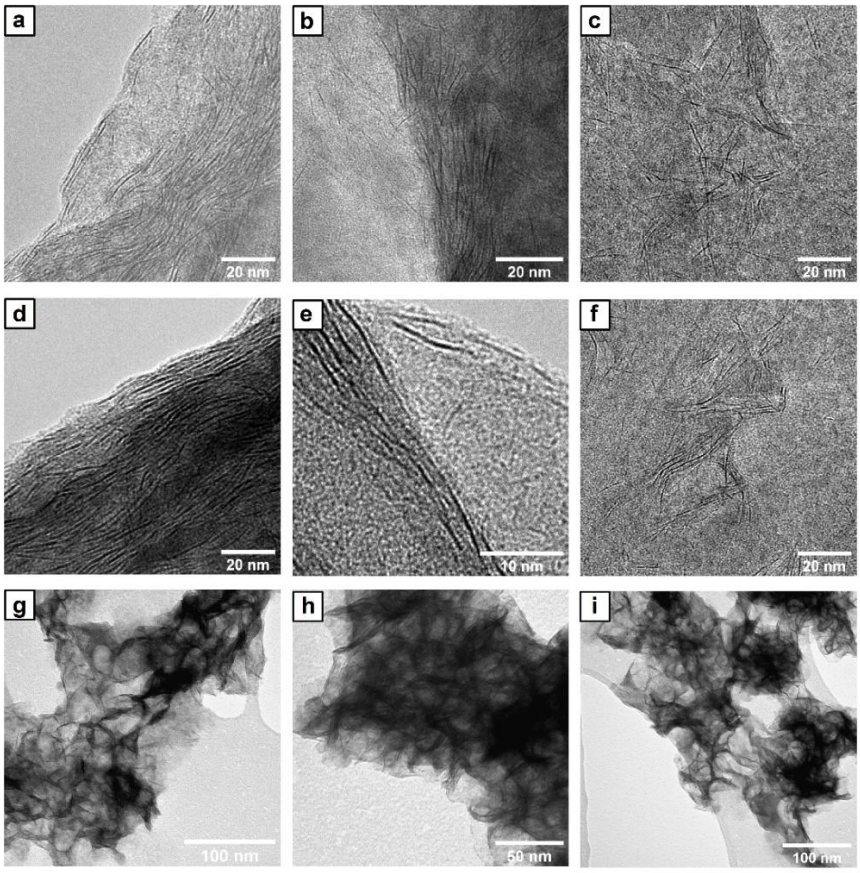


Figure S4. HR-TEM images of A exciton position optimized WS_2 sample (a-c), background optimized WS_2 sample (d-f) and run no. 11 (g-i) as comparison.

A exciton optimized and background optimized sample nanosheet length distribution.

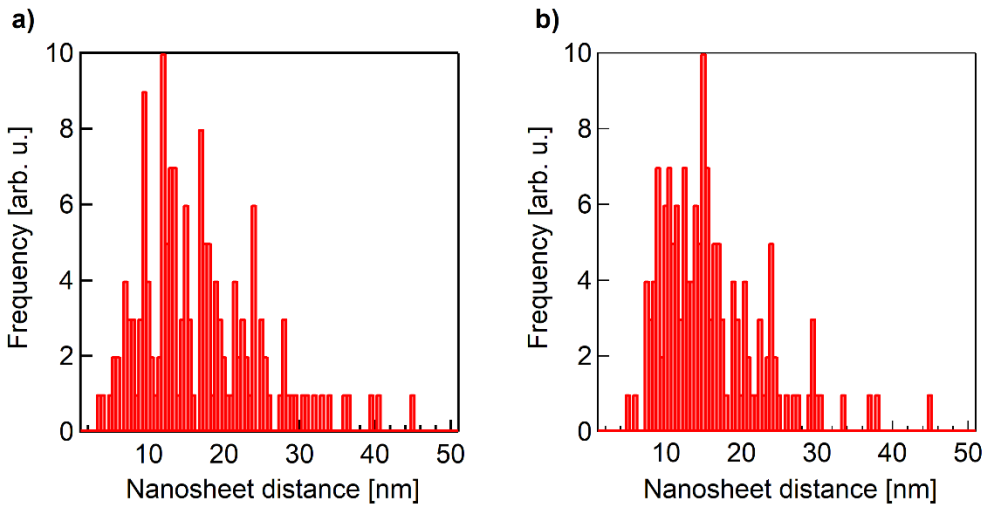


Figure S5. Histogram of the of A exciton position optimized WS_2 sample (a) and background optimized WS_2 sample (b) nanosheet length distribution.

Nanosheet distance distribution for A exciton optimized and background optimized samples.

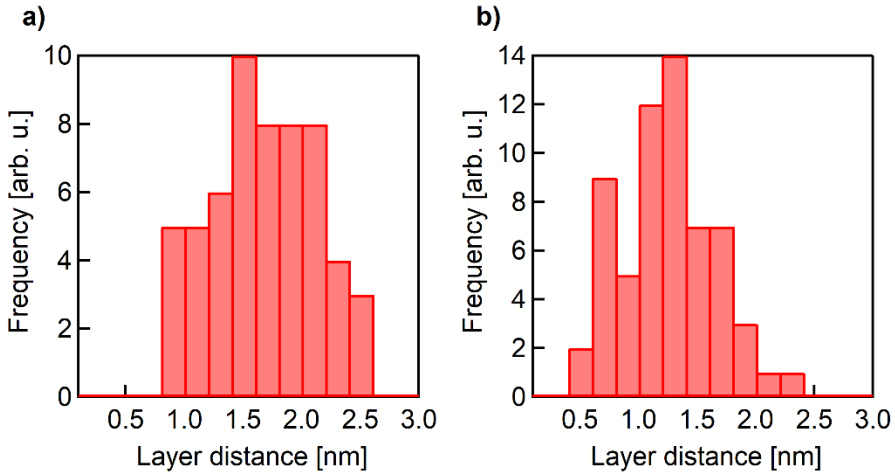


Figure S6. Histogram of the of A exciton position optimized WS_2 sample (a) and background optimized WS_2 sample (b) nanosheet distance distribution.

PXRD of A exciton and background optimized samples.

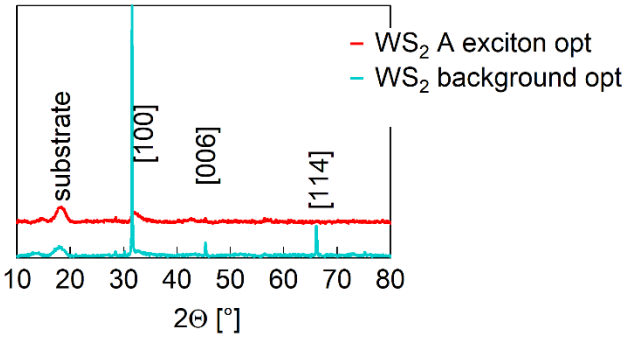


Figure S7. PXRD of A exciton and background optimized samples with assigned reflection (ICDS collection code 202366). The absence of the [002] reflection confirms the monolayer assignation to the samples.

REFERENCES

1. Neath, A. A.; Cavanaugh, J. E., The Bayesian information criterion: background, derivation, and applications. *WIREs Computational Statistics* **2011,** *4* (2), 199-203.
2. Hurvich, C. M.; Tsai, C. L., Regression and Time-Series Model Selection in Small Samples. *Biometrika* **1989,** *76* (2), 297-307.