Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Fine tunable aqueous solution synthesis of textured flexible SnS2 thin films and nanosheets

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Experimental details

Preparation of aqueous solutions of $(NH_4)_4Sn_2S_6{\cdot}3H_2O$: As stated in the main paper precursor solutions for the thin film synthesis can made without initial synthesis of $(NH_4)_4Sn_2S_6{\cdot}3H_2O$ crystals. Alternatively, SnS_2 can directly be dissolved in aqueous $(NH_4)_4S$ and used as precursor solution. In a typical synthesis 2.000 g of $SnCl_4{\cdot}5H_2O$ (purity 98%, Sigma-Aldrich) is dissolved in 80 mL 0.5 M HCl. H_2S (purity 99.5%) is bubbled through in a molar ratio of 1:4 (Sn:S), and yellow amorphous SnS_2 precipitates. The SnS_2 is centrifuged (2 minutes at 6500 rpm) and washed 5 times in MilliQ water. Finally the SnS_2 is dissolved in 20 w% $(NH_4)_4S$ (1:1.5 SnS_2 to $(NH_4)_4S$ ratio *i.e.* excess of 1.5 relative to $(NH_4)_4Sn_2S_6$ stoichiometry) and MilliQ water is added until the desired concentration is reached.

Scotch tape test

To test the film adhesion to the glass substrate a scotch tape test was performed. Scotch tape was adhered to the thin film surface and subsequently pulled off. The film remained on the glass substrate as a testament to the good SnS_2 to glass substrate adherence. Positive results for similar tests have been obtained for MoS_2 and most famously for graphene.[1,2]

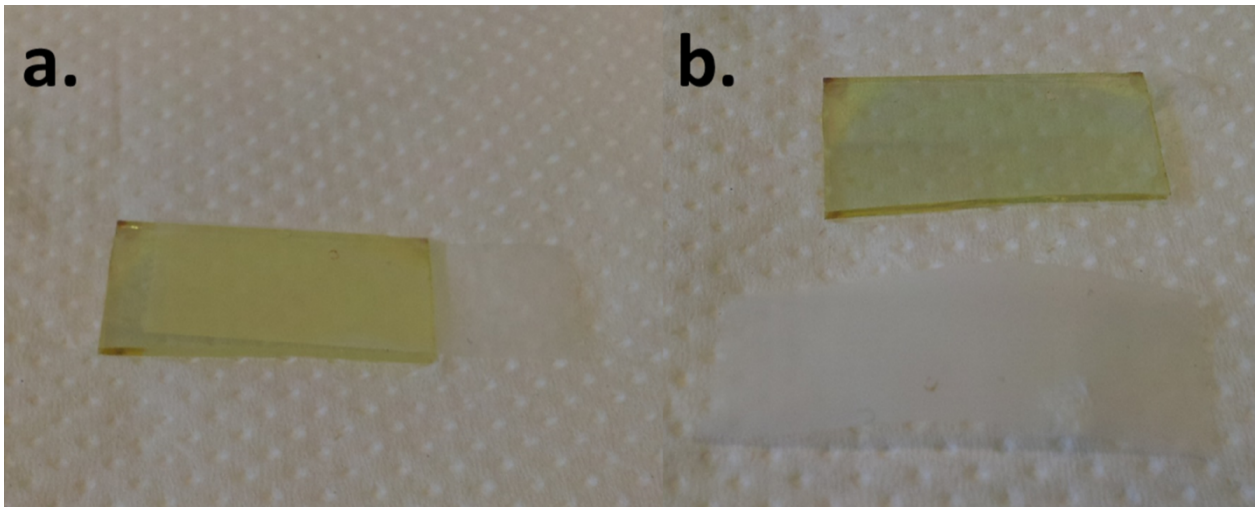

Figure S1. Scotch tape test for the film. a. The film with the adhesive tape applied. b. The film after removal of the tape.

Coherent scattering domains

Using the XRD data presented in Figure 1 (in the main paper), the volume averaged size in the coherent scattering domains were calculated using the Scherer equation.

$$d = \frac{K\lambda}{\beta \cos\theta}$$

Here d is the size of the crystalline domain (crystallite size), K is the Scherer constant, λ the X-ray wavelength, θ is the angular peak position, and β the integral breadth:

$$\beta = \frac{\int I d\theta}{I_{max}}$$

where the numerator is the integrated peak intensity and the denominator is the maximum intensity of the peak.

In the present thin films several effects are likely to contribute to the peak broadening including nanocrystal size, non-uniform strain, and crystal defects such as stacking faults. The latter effect is a particular predominant in layered materials such as SnS_2.[3]

The integral breadth was calculated using Origin8. Assuming spherical nanoparticles (K = 1.123)[4] and ignoring other peak broadening contributions (*e.g.* instrumental broadening, non-uniform stress and stacking faults) the nanocrystal domain size along [001] are shown in the figure below:

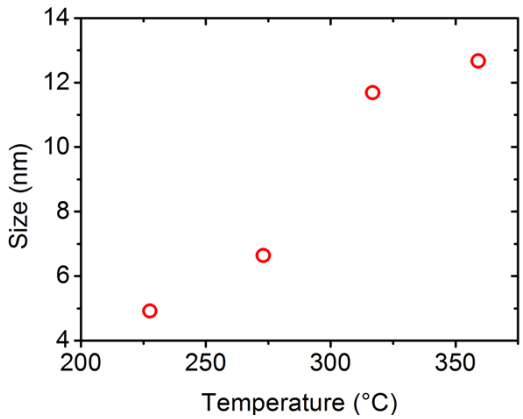

Figure S2. The nanocrystal domain size calculated using the Scherer equation as a function of the annealing temperature.

Determination of PMMA thickness

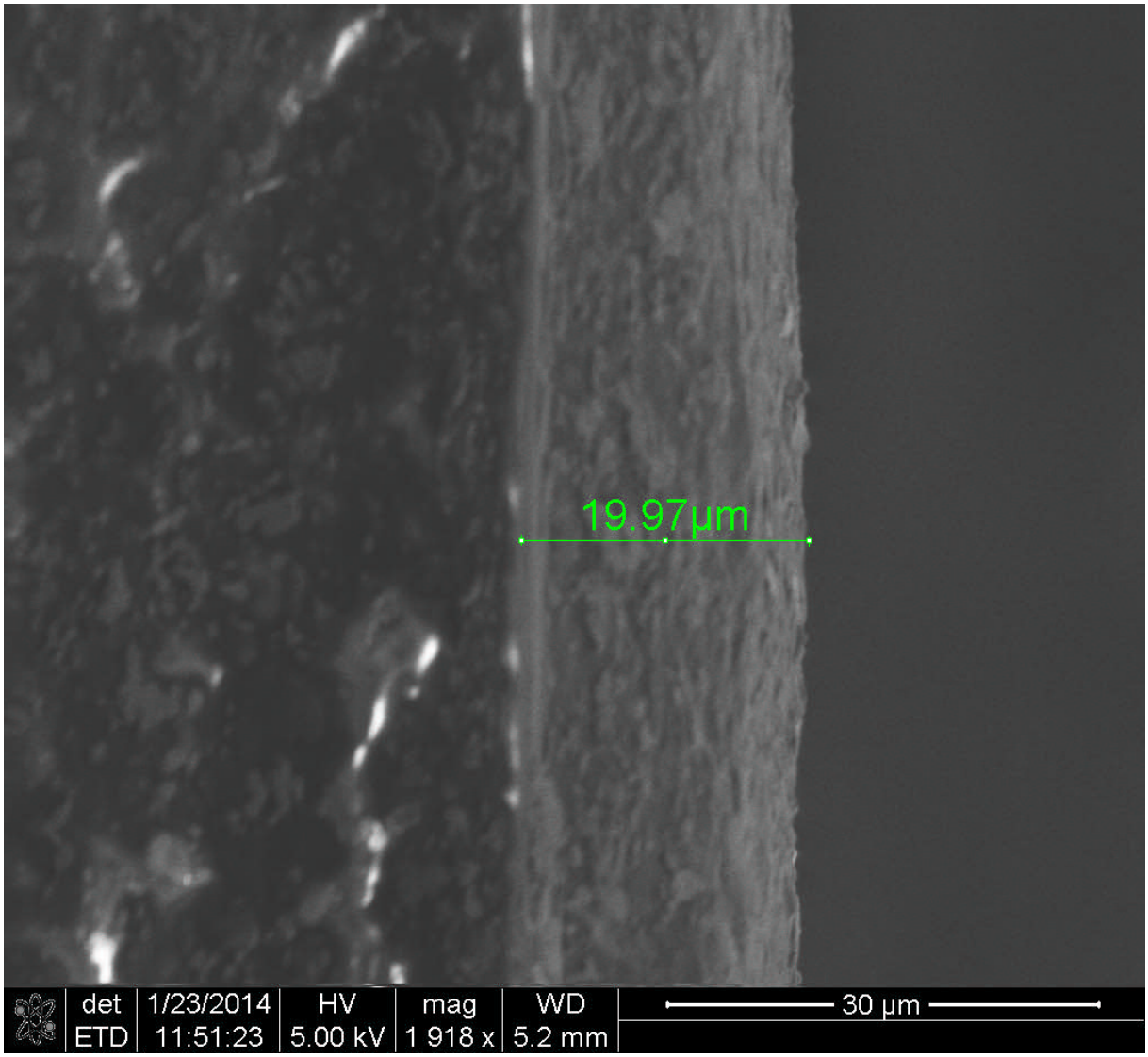

Figure S3. Shows a cross sectional SEM picture of the glass-SnS_2-PMMA structure with the thickness of the PMMA indicated.

Refinement of X-ray reflectivity (XRR) data

A model was fitted to the recorded XRR data using the Global-fit program, and examples of the fits are shown in figure S4 below. Parameters fixed in the refinements are marked *f* in the table S1.

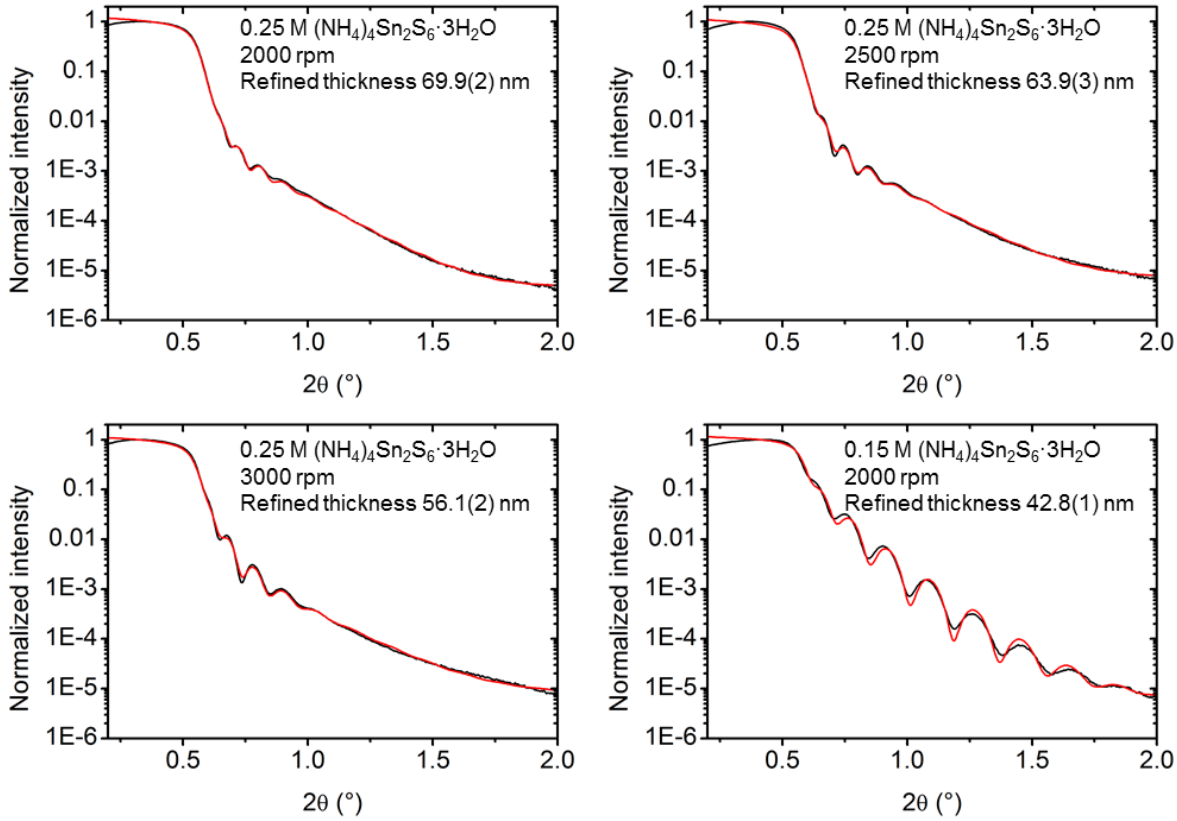

Figure S4. X-ray reflectivity data (solid black line) along with the fitted model (solid red line).

Table S1. Extracted values from refined XRR data presented in Figure S4

$(NH_4)_4Sn_2S_6{\cdot}3H_2O$ concentration	Angular velocity	SnS_2 thickness	Surface roughness	SnS_2 top layer density	SnS_2 bottom layer density	Interface roughness	Substrate density
(M)	(rpm)	(nm)	(nm)	($g{\cdot}cm^{-3}$)	($g{\cdot}cm^{-3}$)	(nm)	($g{\cdot}cm^{-3}$)
0.25	2000	69.9(2)	4.93(3)	3.94(1)	4.57(3)	1.701(6)	2.2*f*
0.25	2500	63.9(3)	4.70(4)	3.97(2)	4.54(3)	1.55(1)	2.2*f*
0.25	3000	56.1(2)	4.37(3)	3.81(1)	4.30(2)	1.43(1)	2.2*f*
0.15	2000	42.8(1)	2.277(18)	4.11(3)	4.57*f*	1.46(2)	2.2*f*

1. K. S. Novoselov, A. K. Geim, S. V Morozov, D. Jiang, Y. Zhang, S. V Dubonos, I. V Grigorieva, and A. A. Firsov, *Sci.* , 2004, **306** , 666.

2. R. F. Frindt, *J. Appl. Phys.*, 1966, **37**.

3. C. Weidenthaler, *Nanoscale*, 2011, **3**, 792.

4. D.-M. Smilgies, *J. Appl. Crystallogr.*, 2009, **42**, 1030.