Supporting Information

Preparation of WS₂-PMMA composite films for optical applications

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Figure S1: Scheme of different transfer procedures for WS_2 into organic PMMA solution: Route B (bottom row) was more successful and applied to produce the films shown in the main manuscript.

After several attempts, a successful transfer of WS_2 -SC-H₂O nanosheets into the NMP-THF environment (the favorable solvent mixture for spin coating) was achieved. The following two approaches were the most prosperous and resulted in stable WS_2 -NMP-THF dispersions.

In details, the WS₂-SC-H₂O dispersion was initially trapped between 5k and 22k g and then topped up to 18 mL with deionized (DI) water and then transferred into twelve 1.5 mL Eppendorf vials. With this sample, the first of the 3 cleaning steps was started. The cleaning and concentrating procedure was found to be efficient and not further modified. The twelve vials were centrifuged for 2h at 18 krpm (\sim 30k g) to sediment the nanosheets as completely as possible. After this step, the supernatant containing most of SC was discarded and the sediment containing WS₂ nanosheets was collected and redispersed in DI water, this time by topping up the sediment only up to 9 mL. This way, we continue the removal of the surfactant from the dispersion as well as gradually increasing the WS₂ concentration. The dispersion was transferred again into six 1.5 mL Eppendorf vials and centrifuged for 2hr at 18 krpm (~30k g). Again, the supernatant containing remaining SC was discarded and the sediment with WS₂ nanosheets was collected and redispersed in DI water, this time by topping up the sediment only up to 6 mL. The dispersion was further transferred into four 1.5 mL Eppendorf vials and for the last time centrifuged for 2hr at 18 krpm (~30 k g). As the last step, the sediment containing WS₂ nanosheets was collected as so called "WS₂ concentrate". The following actual transfer steps of the procedure A (top row) and B (bottom row) will be described separately.

Procedure A (top row): PMMA was separately dissolved in both NMP and THF with a concentration of 30 g/L each (being called PMMA-NMP and PMMA-THF, respectively). The "WS₂ concentrate" dispersion from the last step of the cleaning procedure (described above) was split into two vials and each of them was topped up with PMMA-NMP or PMMA-THF to the volume of 1.5 mL. Dispersions were sonicated in a sonic bath for 5 minutes to ensure elimination of any occurring aggregation in the mixing process. This resulted in 2 dispersions: WS₂-PMMA-NMP and WS₂-PMMA-THF. They can be mixed at the ratio of a choice and then spin coated in order to obtain WS₂ – PMMA films. In this work they were successfully mixed with a ratio of: 5:2 with final volumes of 300-350 μ L.

Procedure B (bottom row): PMMA was separately dissolved in both NMP and THF with a concentration of 30 g/L each (being called PMMA-NMP and PMMA-THF, respectively). This time, both PMMA dispersions were first mixed at ratio of choice (5:2) with a final volume 300-350 μ L and sonicated for 2 minutes. Finally, 5-50 μ L of "W-äS₂ concentrate" was added to the mixture and bath sonicated for 2 minutes resulting in a WS₂ -PMMA-NMP-THF dispersion ready for spin coating.



Figure S2: A) Extinction spectra of THF-PMMA-WS₂ dispersions with different WS₂ content; WS₂ trapped 1-5k g. B) Extinction spectra of WS₂-PMMA films made out of the corresponding dispersions shown in A. C) A-exciton optical density of THF-NMP-WS₂ dispersions and films.

As mentioned above, the addition of 5-50 μ L of "WS₂ concentrate" was tested in order to prepare dispersions of WS₂ suitable for spin coating films. The important point was to avoid aggregation before or during the film formation. Five dispersions with different WS₂ concentrations in the mixture were initially tested. The extinction spectra are shown in Figure S4. Their optical densities (OD) at the A-exciton were ~2, 5, 15, 20 and 80. After the spin coating, only 4 films were properly formed, and their OD at the A-exciton were 0.01, 0.05, 0.1 and 0.15 (extinction spectra see Figure S4B). This means that the OD at A-exciton region of the film is always significantly lower than that of the initial dispersion. This relationship is presented at Figure S4C and is a valuable information when a specified OD of the film is needed. However, this illustrates that it will be a great challenge to increase the WS₂ loading in the film further, as no homogeneous films could be formed for higher WS₂ concentrations than $OD_A=20$ in the dispersion corresponding to a concentration of 2.8 g/L when we assume an extinction coefficient at the A-exciton of ~7 Lg⁻¹cm⁻¹.¹

3. Calculation of nanosheet dimensions from optical extinction spectra

The arithmetic mean length of the nanosheets, <L> and the arithmetic mean nanosheet layer, <N> were calculated from the ratio of the local maximum at 290 nm to the local minimum at 235 nm (Ext₂₃₅/Ext₂₉₀, Equation 1) and the wavelength of the A-exciton (λ_A , Equation 2), respectively.¹⁻² Note that the A-exciton position was determined from the smoothed second derivative as detailed (see ¹⁻³), since this method partially compensates artificial shifts which can arise from superposition of scattering.

$$L(nm) = \frac{2.3 - Ext_{235}/Ext_{290}}{0.02Ext_{235}/Ext_{290} - 0.0185} \qquad Equation \ l$$

$$\langle N \rangle = 6.35 \times 10^{-32} e^{\lambda_A(nm)/8.51}$$
 Equation 2

4. Atomic Force Microscopy on WS₂-SC-H₂O dispersions



Figure S3: AFM images of WS₂ deposited from the aqueous surfactant dispersions. 5-22k g – top row; 1-5k g – bottom row.

Both the 1-5k g and 5-22k g WS₂-SC dispersions were characterised by atomic force microscopy (AFM) in order to confirm the good quality of nanosheets and sizes/thicknesses derived from the spectroscopic metrics. All representative images displayed above in Figure S3 are in the same scale. Lateral sizes of the sheets in the 5-22k g dispersion range from 60-80 nm and from 75-150 nm in the 1-5k g dispersion. Considering cantilever broadening and pixilation effects, this agrees well with the sizes determined from metrics. The apparent AFM thickness of the sheets in the 5-22k g dispersion ranges from 3-8 nm with the majority of nanosheets being ~3 nm thick. Note that 3 nm is the reported apparent AFM thickness of surfactant-exfoliated transition metal dichalcogenides and that one layer is seen as ~1.9 nm.^{2, 4} In the 1-5k g dispersion, thicknesses from 3-12 nm are observed. Overall, AFM agrees well the lateral sizes and thicknesses derived from the metrics.

The nanosheet lateral size and layer number was evaluated on a statistical basis by AFM (see figure S4) using established corrections for nanosheet lateral size³ and layer number from step height analysis.^{2, 4}



Figure S4: Length and height histograms corresponding to $WS_2 <L>$ and <N> in dispersions: 5-22k g – top row; 1-5k g – bottom row.



5. 2nd derivatives. comparison between WS₂-SC-H₂O / WS₂-THF-NMP / WS₂-PMMA.

Figure S5: 2nd derivatives of the A-exciton region of the extinction spectra. Left) 1-5k g WS₂ sheets in H₂O-SC (black), THF-NMP-PMMA (red) and WS₂-PMMA film (blue). Right) 5-22k g WS₂ sheets in H2O-SC (black), THF-NMP-PMMA (red) and WS₂-PMMA film. Spectra are offset for clarity.

 2^{nd} derivatives of the A-exciton region of LPE WS₂ are known to be indicators of the monolayer and fewlayer contribution in the given dispersion.² Figure S5 shows 2^{nd} derivatives in this region for WS₂-SC dispersion, WS₂-NMP-THF-PMMA dispersion as well as WS₂-PMMA film for larger (1-5k g, left) and smaller (5-22k g, right) WS₂ sheets, respectively. It is clearly visible that the peaks red-shifts after transfer into the organic solvent-PMMA environment and blueshifts again after the film deposition to the position close to the initial dispersion.





Figure S6: A) Photoluminescence excitation emission map of WS_2 -PMMA film infused with WS_2 nanosheets trapped between 1-5k g. B) Normalised single emission photoluminescence spectra (430 nm excitation) of the initial WS_2 -SC dispersion and the WS_2 -PMMA film

Photoluminescence excitation-emission maps were acquired at the same conditions as for the liquid dispersion of WS₂ (Figure 2 in the main manuscript). A map of the film based on the monolayer-rich dispersion is displayed in Figure 2E in the main manuscript. Here (Figure S6A) we present corresponding map for the film prepared from the larger nanosheet dispersion. PL features are again visible, but much fainter as for the 5-22k g film due to the lower content of WS₂ monolayers. A comparison of the single emission spectra of film and initial dispersion (Figure S6B) shows that, in analogy to the 5-22k g sample, the emission is slightly blue-shifted and narrowed compared to the initial surfactant dispersion.

7. Scanning Electron Microscopy on WS₂-PMMA film

To investigate the uniformity of the film over larger surface areas, scanning electron microscopy (SEM) was carried out. The samples were characterised using a Carl Zeiss Ultra Plus scanning electron microscope. A low accelerating voltage of 2 kV was used to capture the

images as the samples show poor conductivity due to the insulating polymer matrix. The images were taken at a working distance of 3.1 mm. Representative images for films infused with a different nanosheets sizes are shown on Figure S7. They confirm the films are very uniformly formed over surface of >10 um² which is sufficient for many optical applications.

Figure S7: SEM – characterisation of the films surface; 5-22 kg – top row, 1-5 kg – bottom row



Experimental data collected during measurements for both film and dispersion were fitted according to the nonlinear beam propagation model (equation 1), where I is the light intensity, z' is propagation distance and the total absorption α is a sum of linear absorption α_0 and nonlinear absorption coefficient β_{eff} (equation 2).

 $\frac{dI(z')}{dz'} = -\alpha(I)I$ (equation 1) $\alpha(I) = \alpha_0 + \beta_{eff}I$ (equation 2)

This standard open Z-scan model shows excellent fitting for all the z-scan curves presented in this study. Fitted plots of experimental Z-scan spectra are shown in Figure 4A&B, representative raw data and respective fits are presented in Figure S8.



Figure S8: Transmission measured with OA z-scan (scatter) and fitted plots (lines) for 2 different energies of 1μ J and 15μ J.

Supporting References

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