Low-defectiveness exfoliation of MoS_2 nanoparticles and their embedment in hybrid light-emitting polymer nanofibers

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Electronic Supplementary Information

Experimental Details

MoS_2 exfoliation. Bulk MoS_2 powder (99%, < 2 μm in size, Sigma Aldrich) was dispersed in *N*-methyl-2-pyrrolidone (NMP) (99.5% anhydrous, Sigma Aldrich) with a concentration of 2 mg mL^{-1} and sonicated for 8 hours, at room temperature, using a bath sonicator (CEIA, CP102 digit) at a constant power of 200 W. Following ultrasonication, the obtained product was centrifuged at 1000 rpm for 45 minutes and the supernatant was used for further characterization. The concentration of the dispersion was measured by completely removing the solvent. The dispersion was centrifuged at 14,000 rpm for 45 minutes until the complete sedimentation of MoS_2, then the transparent supernatant was collected and the residual solvent was removed by storing under vacuum for 24 h. Finally, the sediment was weighted and dispersed in NMP at known concentration.

Electrospinning. For realizing hybrid nanofibers, MoS_2 was firstly dispersed in NMP at the concentration of 3.4 mg mL^{-1} and ultrasonicated for 1 hour prior electrospinning. Fibers were obtained by dissolving 350 mg of poly(methyl methacrylate) (PMMA) in 1 mL MoS_2 /NMP dispersion, stirring and sonicating the so-achieved solution for 4 hours. At PMMA concentrations below 350 mg mL^{-1}, fibers were not uniform, showing beaded morphology. The electrospinning process underwent extensive optimization, varying the applied voltage in the range 10-20 kV, the needle-to-collector distance in the range 5-20 cm and the flow rate in the range 0.2-2 mL h^{-1}. Finally, the process was carried out by a syringe with a 21 gauge stainless steel needle, an applied voltage of 14 kV, a needle to collector distance of 15 cm and a flow rate of 0.5 mL h^{-1}. Both a flat plate and a rotating collector (disk with 0.8 cm width, 8 cm diameter and speed 4000 rpm) were used to obtain randomly oriented and aligned nanofibers, respectively.

Spectroscopy. Ultraviolet-visible (UV-Vis) absorption spectra were collected from MoS_2 dispersions and aligned, free-standing mats of fibers by using a Lambda 950 spectrophotometer (Perkin Elmer Inc.). Fluorescence and transmission micrographs were acquired by an inverted microscope Eclipse Ti equipped with a confocal A1R-MP system (Nikon), using an Argon ion laser (excitation wavelength, $\lambda = 488$ nm). The sample emission was collected by a 20× (Numerical Aperture, NA = 0.50, Nikon) and a 60× (oil immersion NA = 1.40, Nikon) objective and the fluorescent signal was detected by a spectral detection unit equipped with a multi-anode photomultiplier (Nikon). Confocal microscopy was performed on both dried drop-casted MoS_2 dispersions and fibers, deposited on glass substrates. A 3D reconstruction of fibers was obtained in *Z*-stack mode with a step size of 0.3 μm.

Micro-Raman experiments were carried out with a Renishaw InVia spectrometer equipped with a confocal optical microscope and a 532 nm excitation laser. The spectral resolution of the system is 1 cm^{-1}. The micro-Raman spectra was acquired with a 50× objective (NA 0.8), a laser power of 1 mW, and an acquisition time of 2 s. The peak fitting was carried out with a Levenberg-Marquardt algorithm, employing a Voigt function for the evaluation of the peak parameters.

Morphological characterization. Morphological analysis of exfoliated MoS_2 and of electrospun fibers was performed by scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM, FEI Nova NanoSEM 450). The microscopy was equipped with an energy dispersive X-ray (EDS) detector and operating at acceleration voltages of 6-20 kV. Samples of exfoliated MoS_2 were prepared by drop-casting on a Si surface. All the samples were metallized by thermal evaporation (chromium or aluminum, PVD75, Kurt J. Lesker Co.) prior to SEM analysis. Transmission electron microscopy (TEM) images were acquired with a JEOL Jem1011 microscope operating at an accelerating voltage of 100 kV. For this analysis, few

drops of MoS_2 dispersion were drop-casted onto carbon-coated copper grid (300 mesh). TEM images were collected and processed by using the Gatan Microscopy Suite (GSM) software.

Confocal fluorescence lifetime imaging microscopy (FLIM). PL lifetime measurements were performed by an inverted microscope with confocal head (TCS SP5, Leica Microsystem) and a 40× objective (NA=1.24). A 470-nm pulsed diode laser operating at 40 MHz was used as excitation source. The fluorescence intensity from light-emitting fibers was collected in the 480-600 nm range by a photomultiplier tube interfaced with a time-correlated single photon counting setup (PicoHarp 300, PicoQuant, Berlin). FLIM acquisitions lasted until an average of 10^2-10^3 photons were collected in each pixel.

Waveguiding. Waveguiding was studied by using a micro-photoluminescence system, based on an inverted microscope (IX71, Olympus) equipped with a 20× objective (NA = 0.50, Olympus) and a charge coupled device (CCD) detector. The sample photoluminescence was excited by a continuous wave diode laser (λ = 405 nm), coupled to the microscope by a dichroic mirror and focused on the sample through the microscope objective (spot diameter about 10 μm). Individual freestanding fibers were suspended on a holder with a slot of 0.5 cm. The laser beam was focused on a single emissive fiber and fluorescence images were acquired using the CCD camera. After the excitation, part of the light emitted by MoS_2 was coupled into the fiber and then guided. Therefore, using the acquired images, the optical losses were evaluated by measuring the intensity of the light scattered from fiber surface as a function of the distance, *d*, from the exciting laser spot.

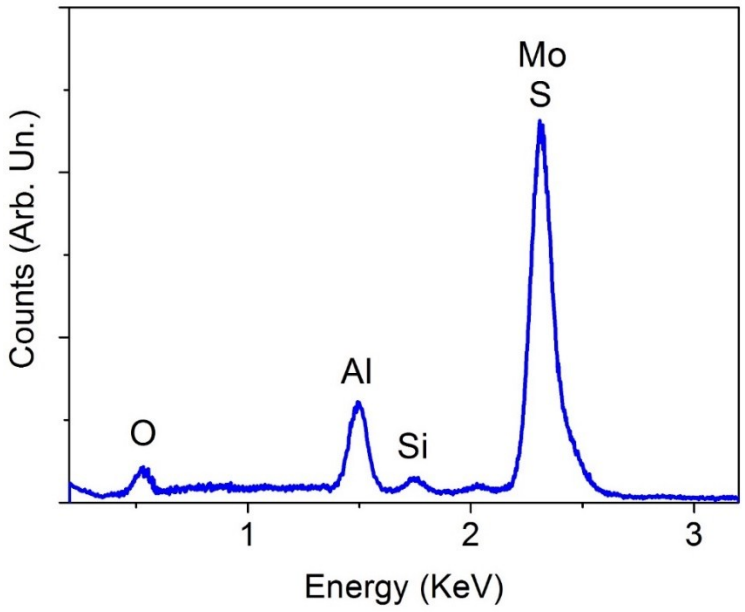

Fig. S1. EDS profile of drop-casted MoS_2 dispersion. Silicon belongs to the substrate on which fibers are deposited, while aluminum was thermally evaporated onto the fibers for SEM imaging.

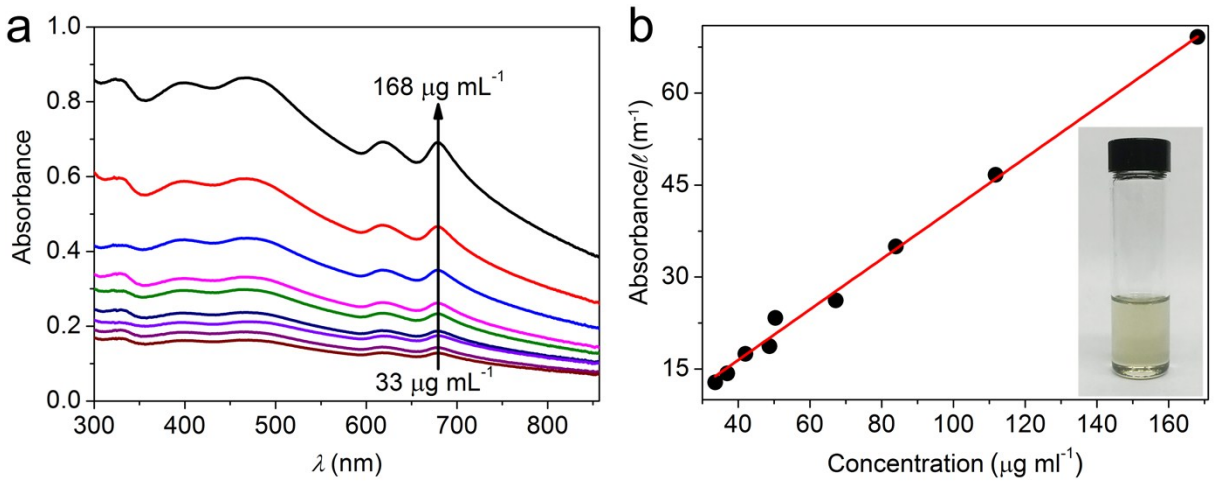

Fig. S2. (a) Absorbance spectra of MoS_2 dispersions at different concentration. From bottom to top, concentration = 33 μg mL^{-1}, 37 μg mL^{-1}, 42 μg mL^{-1}, 48 μg mL^{-1}, 50 μg mL^{-1}, 67 μg mL^{-1}, 84 μg mL^{-1}, 111 μg mL^{-1}, 168 μg mL^{-1}. (b) Lambert-Beer linear plot for MoS_2 dispersions. The slope of the line provides the extinction coefficient at $\lambda_{678\,nm}$: 412 mL mg^{-1} m^{-1}. l is the optical path length. The inset shows a MoS_2 dispersion in NMP (1:10) with a concentration of 84 μg mL^{-1}.

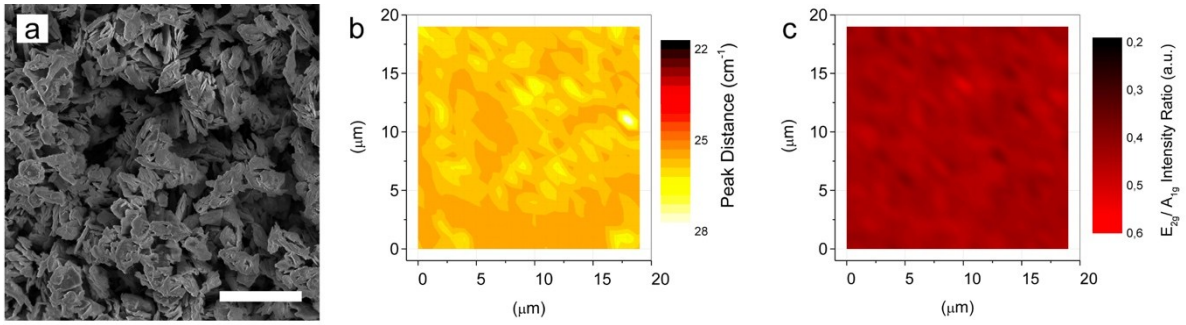

Fig. S3. (a) SEM micrograph of the bulk MoS_2 powder. Scale bar = 5 μm. Maps of the Raman mode spacing (b) and of the E_{2g}-A_{1g} intensity ratio (c) acquired on bulk MoS_2.

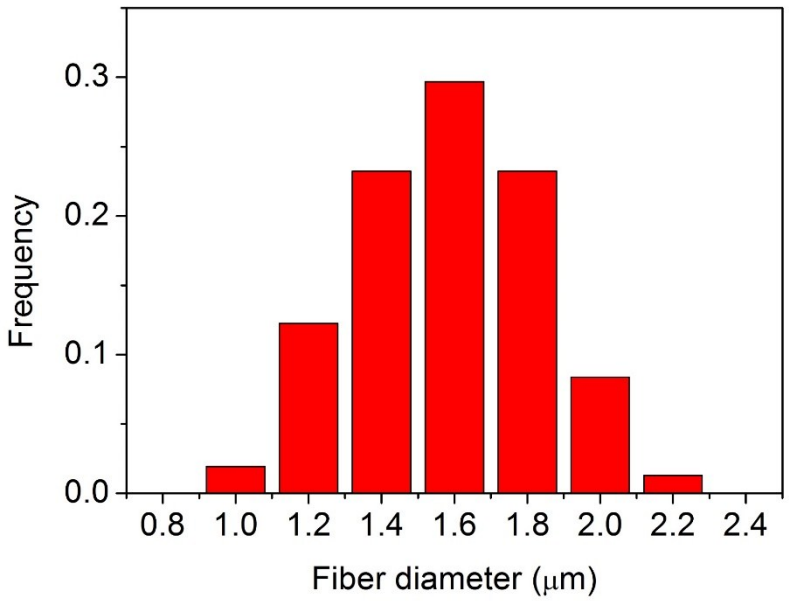

Fig. S4. Diameter distribution of the hybrid MoS_2-polymer fibers.