**Electronic Supplementary Information**

# Phase-preserved fragmentation of bulk $WS_2$ to nanoparticles in charged water microdroplets

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**S1. Materials.**

Tungsten disulfide ($WS_2$) sample was purchased from Aldrich (powder < 2micron, 99%, Cat.: 24,363-9, Lot.: 30175-074). Ultrapure Milli-Q water (18.5 MΩ·cm at 25 °C) was employed throughout all experiments.

**S2. Synthesis of two-dimensional $WS_2$ sheets.**

Bulk $WS_2$ were dispersed in Milli-Q water to form suspensions, which were then subjected to ultrasonication in an ultrasonic bath (40 kHz, 100 W, 2 min) to enhance dispersion and break up agglomerates. Subsequently, the suspensions were centrifuged using a Remi RM-03 Plus at 10 000 rpm for 2 min to achieve preliminary size separation, removing larger particulates and enriching finer and mid-range microparticles. This process was repeated three times. A final gentle centrifugation step (1000 rpm, 30 sec) was performed to obtain a stable suspension.

**S3. Electrospray deposition experiments.**

A custom-built electrospray setup as shown in Fig. S2 was employed to generate microdroplets. Suspensions were delivered through a gastight 0.5-mL Hamilton syringe fitted with a 22-gauge needle (inner diameter 413 µm), connected via a union to a 50-µm (inner diameter) fused silica capillary. The syringe needle was connected to the high voltage power supply, and the carbon-coated copper TEM grid with 300 mesh was kept on the grounded plate collector. Flow rates were precisely controlled using a stepper motor (400 steps per rotation). Deposition experiments were conducted under ambient conditions (25 °C and 50-60 % relative humidity) for 1 h. The polyimide coated fused silica capillary was procured from Polymicro Technologies™, Molex, USA, while other components like union connector, PEEK tubing, ferrules were purchased from IDEX Health & Science, USA.

**S4. Characterization.**

Digital photographs of the bulk sample and experimental setup were acquired using the telephoto camera of an iPhone 14 Pro Max. Micro-sized $WS_2$ particles were imaged using a Thermo Fisher Scientific Verios G4 UC high-resolution field emission scanning electron microscope (FESEM) operated at an accelerating voltage of 10 kV and emission current of 0.10 nA. Samples on aluminum substrates were coated with a 0.2-nm gold layer using a Quorum Q150T S plus sputter coater to enhance conductivity for FESEM imaging. Glow

discharge was used for carbon-coated copper TEM grids to eliminate unwanted impurities and enhance surface hydrophilicity using the Quorum GloQube Plus. Thermofischer Talos™ F200i transmission electron microscope (TEM) was used at an accelerating voltage of 200 kV with low electron flux density, for imaging. All samples are dried under vacuum in a desiccator. WiTec (currently Oxford) alpha 300s machine with 1800 g/mm grating is used for Raman measurement. For Raman measurement 532 nm laser is used with 5 sec integration and 10 accumulations. Conducting side of ITO glass slide is used for collecting nanoparticles for Raman measurement. ITO slide was connected via conducting copper tape to grounding (Fig. S11g). Total 18h of spray was done to get quantity for Raman measurement. For FWHM, we performed quantitative Lorentzian peak fitting on the for all three samples.

**S5. Thermodynamically stable phase by Wulff construction**.

The equilibrium shape is determined by minimizing the total energy:

$$\gamma_{total} = \sum \gamma_{hkl}.A_{hkl}$$

$\gamma_{hkl}$ = surface energy density

$A_{hkl}$ = Area of that phase

Faces with the lowest surface energy = largest face on crystal.[1]

**T1.** Table of DigitalMicrograph processed d-spacing with assigned (hkl) plane follow format

| d-spacing obtained from DigitalMicrograph Analysis | Assigned (hkl) plane |
|---|---|
| 0.31-0.37 nm | (004) |
| 0.25-0.27 nm | (100)/(010) |
| 0.20 nm | (006)/(104) |
| 0.18 nm | (105) |

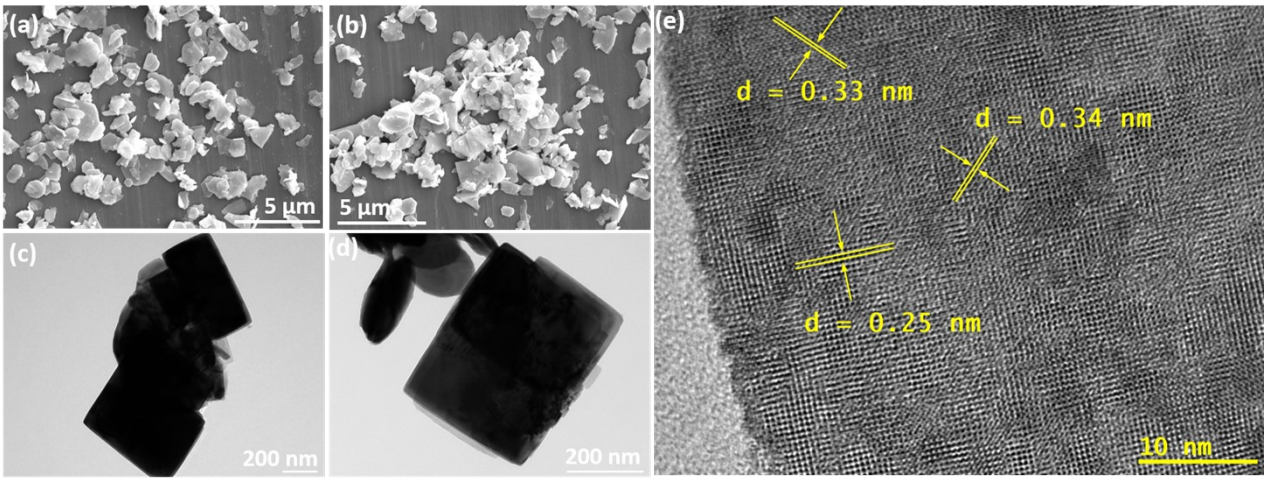



**Fig. S1.** (a, b) Field emission scanning electron microscopy (FESEM) image (c, d) Large area Transmission electron microscope (TEM) image (e) DigitalMicrograph processed high-resolution TEM (HRTEM) image with calculated d spacing of two-dimensional $WS_2$ (before spray).

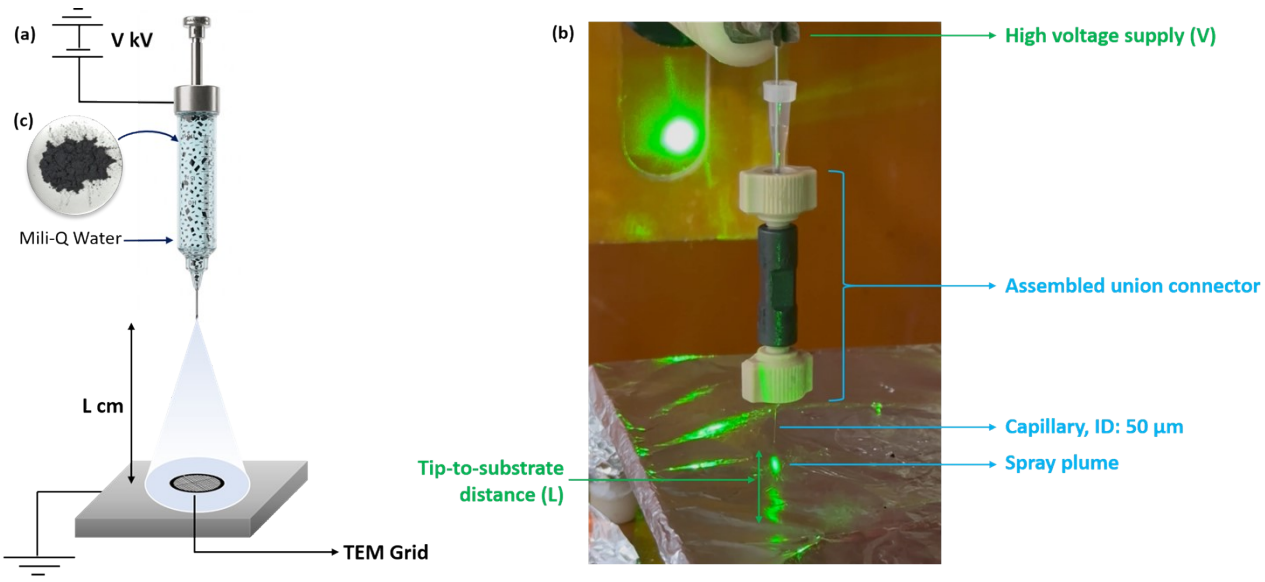



**Fig. S2.** (a) Schematic diagram (b) Photograph showing the different components of the home-built electrospray set-up used for electrospraying. A TEM grid was kept on the substrate below the tip of the capillary at different tip-to-substrate distances. The spray plume was visualized by a green laser. Reflection of the laser light from the aluminium foil is seen. (c) Optical image of the Bulk $WS_2$.

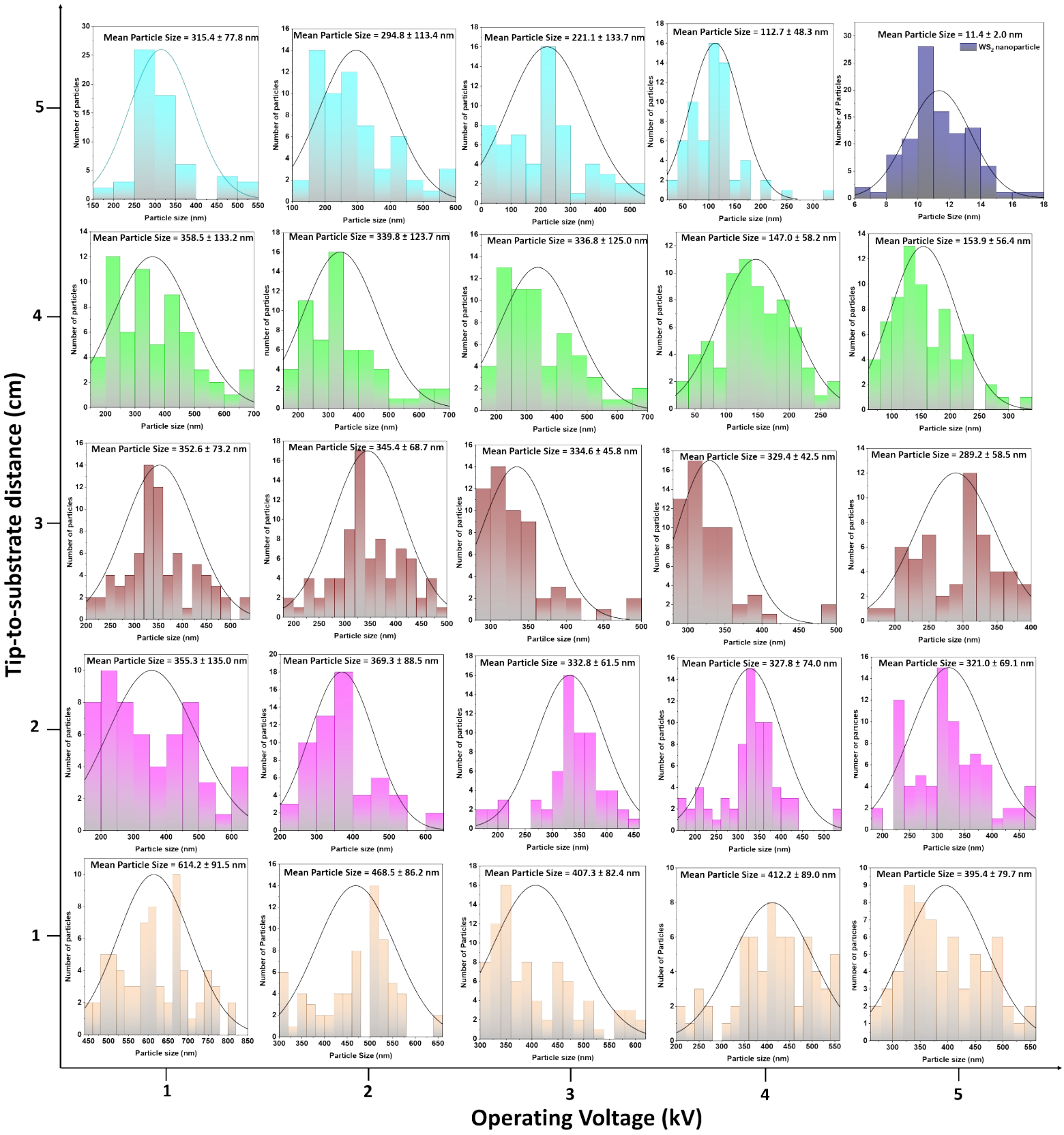

Tip-to-substrate distance (cm)
5
4
3
2
1
Mean Particle Size = 315.4 ± 77.8 nm
Mean Particle Size = 294.8 ± 113.4 nm
Mean Particle Size = 221.1 ± 133.7 nm
Mean Particle Size = 112.7 ± 48.3 nm
Mean Particle Size = 11.4 ± 2.0 nm
WS2 nanoparticle
Mean Particle Size = 358.5 ± 133.2 nm
Mean Particle Size = 339.8 ± 123.7 nm
Mean Particle Size = 336.8 ± 125.0 nm
Mean Particle Size = 147.0 ± 58.2 nm
Mean Particle Size = 153.9 ± 56.4 nm
Mean Particle Size = 352.6 ± 73.2 nm
Mean Particle Size = 345.4 ± 68.7 nm
Mean Particle Size = 334.6 ± 45.8 nm
Mean Particle Size = 329.4 ± 42.5 nm
Mean Particle Size = 289.2 ± 58.5 nm
Mean Particle Size = 355.3 ± 135.0 nm
Mean Particle Size = 369.3 ± 88.5 nm
Mean Particle Size = 332.8 ± 61.5 nm
Mean Particle Size = 327.8 ± 74.0 nm
Mean Particle Size = 321.0 ± 69.1 nm
Mean Particle Size = 614.2 ± 91.5 nm
Mean Particle Size = 468.5 ± 86.2 nm
Mean Particle Size = 407.3 ± 82.4 nm
Mean Particle Size = 412.2 ± 89.0 nm
Mean Particle Size = 395.4 ± 79.7 nm
Number of particles
Particle size (nm)
1
2
3
4
5
Operating Voltage (kV)

**Fig. S3.** Particle size distribution profiles of $WS_2$ as a function of applied potential (in kV) and tip-to-substrate distance (in cm). The applied potential was varied from 1 to 5 kV and tip-to-substrate distance was varied from 1 to 5 cm. The potential and distance values for an experiment correspond to the centre of the particle size distribution profile. As can be seen, large L and V result in nanoparticles.

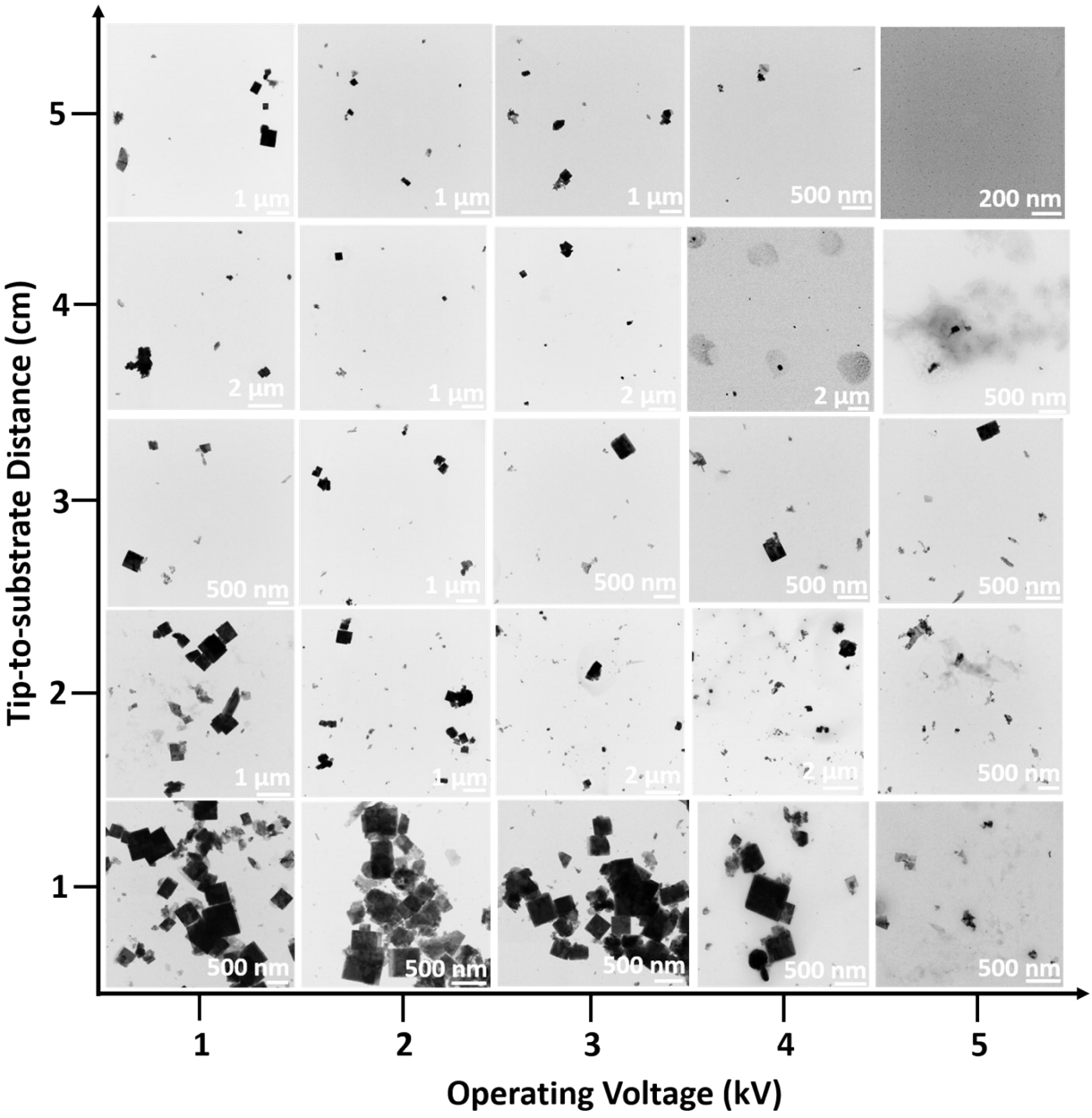
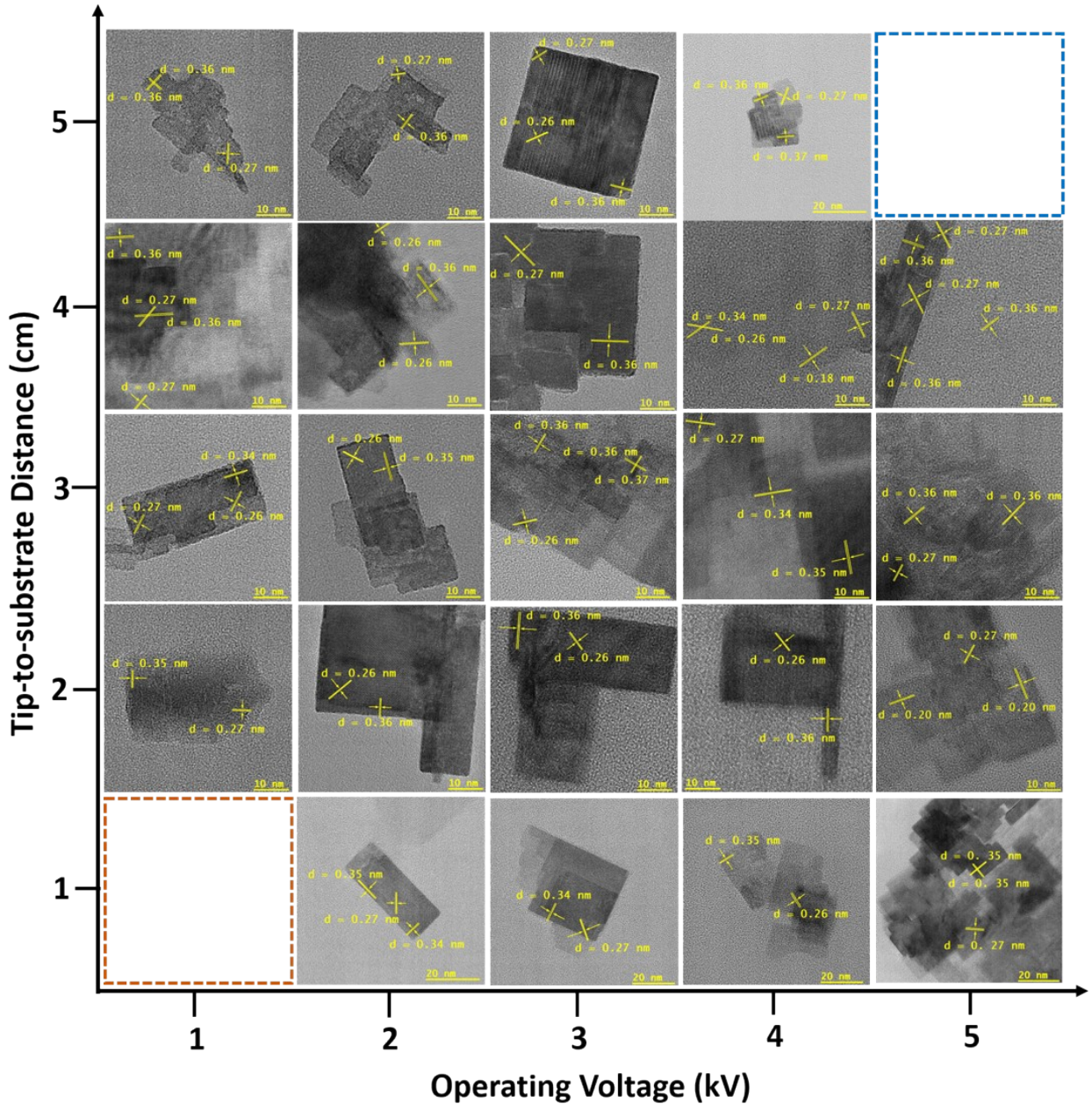


**Fig. S4.** Large area bright field TEM images showing the disintegration pathway of two-dimensional $WS_2$ sheets to particles as a function of applied potential (in kV) and tip-to-substrate distance (in cm). The applied potential was varied from 1 to 5 kV and tip-to-substrate distance was varied from 1 to 5 cm. The potential and distance values for an experiment correspond to the centre of the TEM image. As can be seen, large L and V result in nanoparticles.



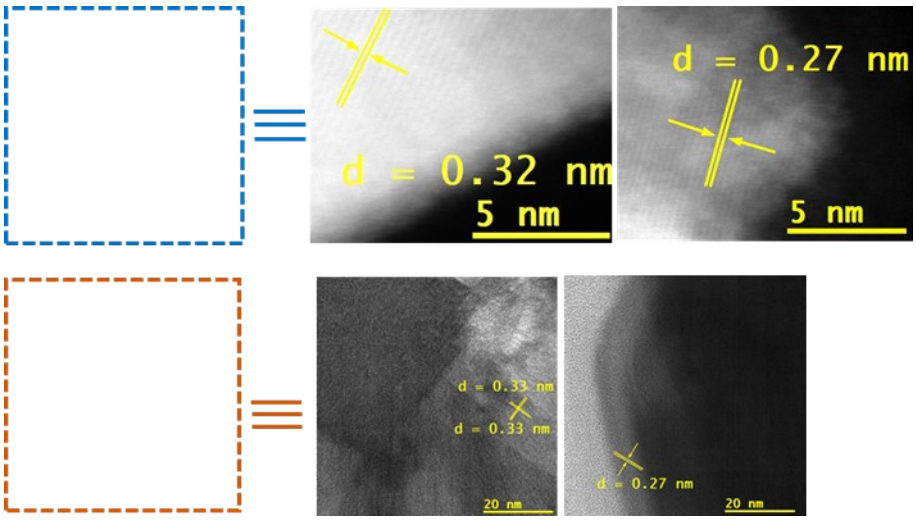



**Fig. S5.** DigitalMicrograph processed High resolution TEM (HRTEM) images showing the disintegration pathway of two-dimensional $WS_2$ sheets to particles as a function of applied potential (in kV) and tip-to-substrate distance (in cm). The applied potential was varied from 1 to 5 kV and tip-to-substrate distance was varied from 1 to 5 cm. The potential and distance values for an experiment correspond to the centre of the HRTEM image. As can be seen, large L and V result in nanoparticles. Images corresponding to (1,1) and (5,5) are presented separately below.

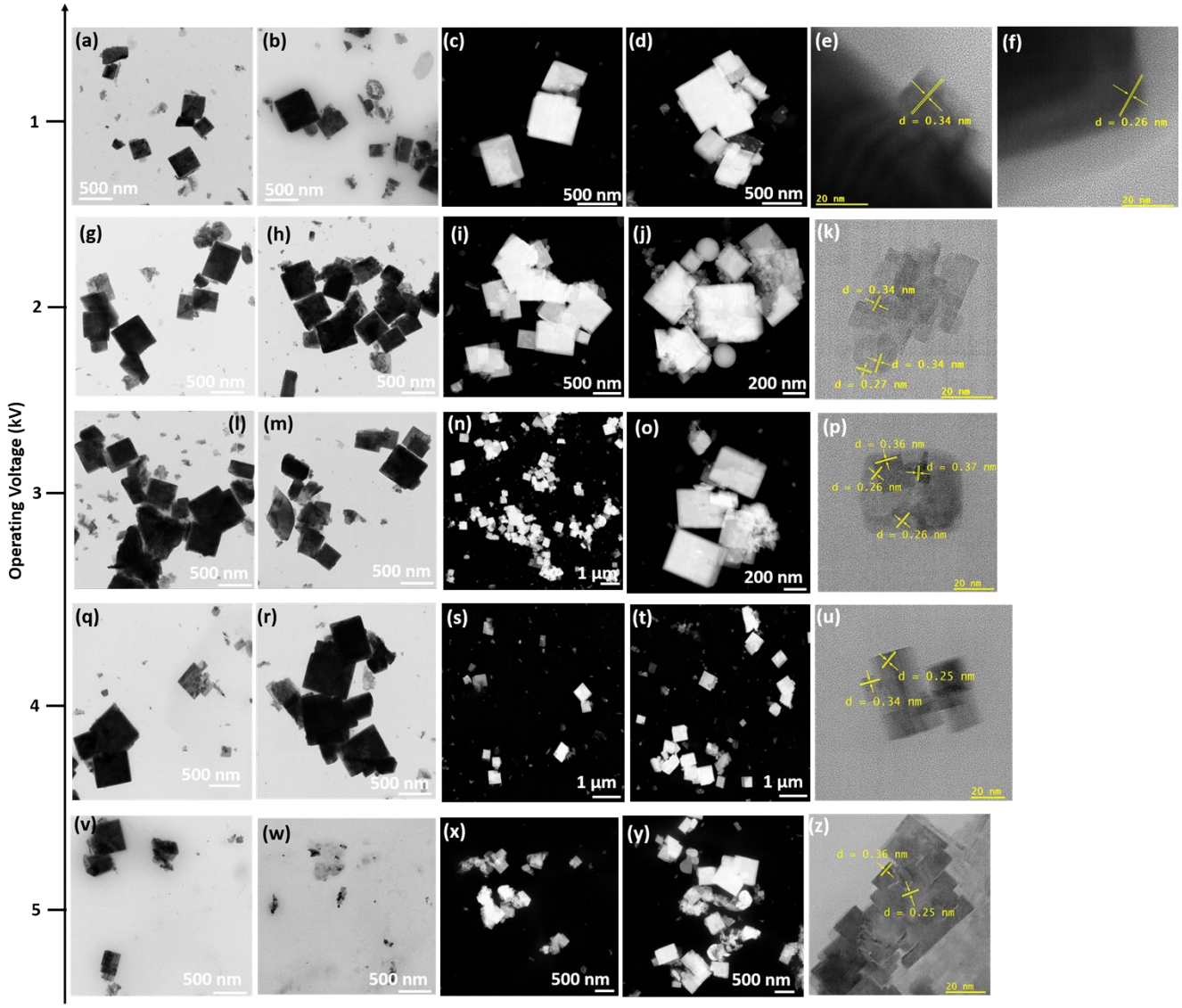



**Fig. S6.** Large area TEM (a, b, g, h, l, m, q, r, v, w), HAADF-STEM (c, d, i, j, n, o, s, t, x, y) and DigitalMicrograph processed HRTEM images (e, f, k, p, u, z) at the applied potential, V = 1-5 kV and tip-to-substrate distance, L = 1 cm.

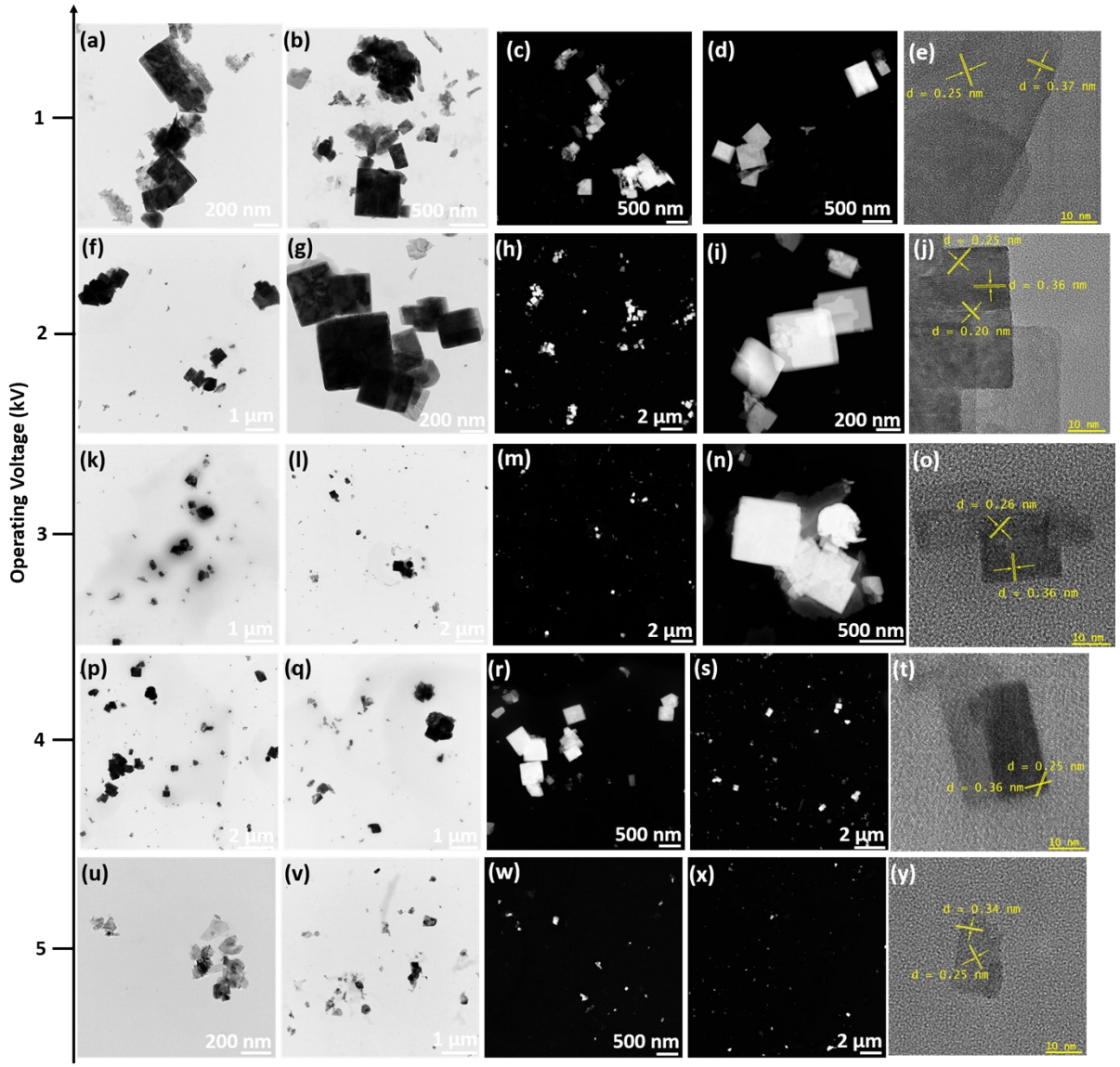



**Fig. S7.** Large area TEM (a, b, f, g, k, l, p, q, u, v), HAADF-STEM (c, d, h, i, m, n, r, s, w, x) and DigitalMicrograph processed HRTEM images (e, j, o, t, y) at the applied potential, V =1-5 kV and tip-to-substrate distance, L = 2 cm.

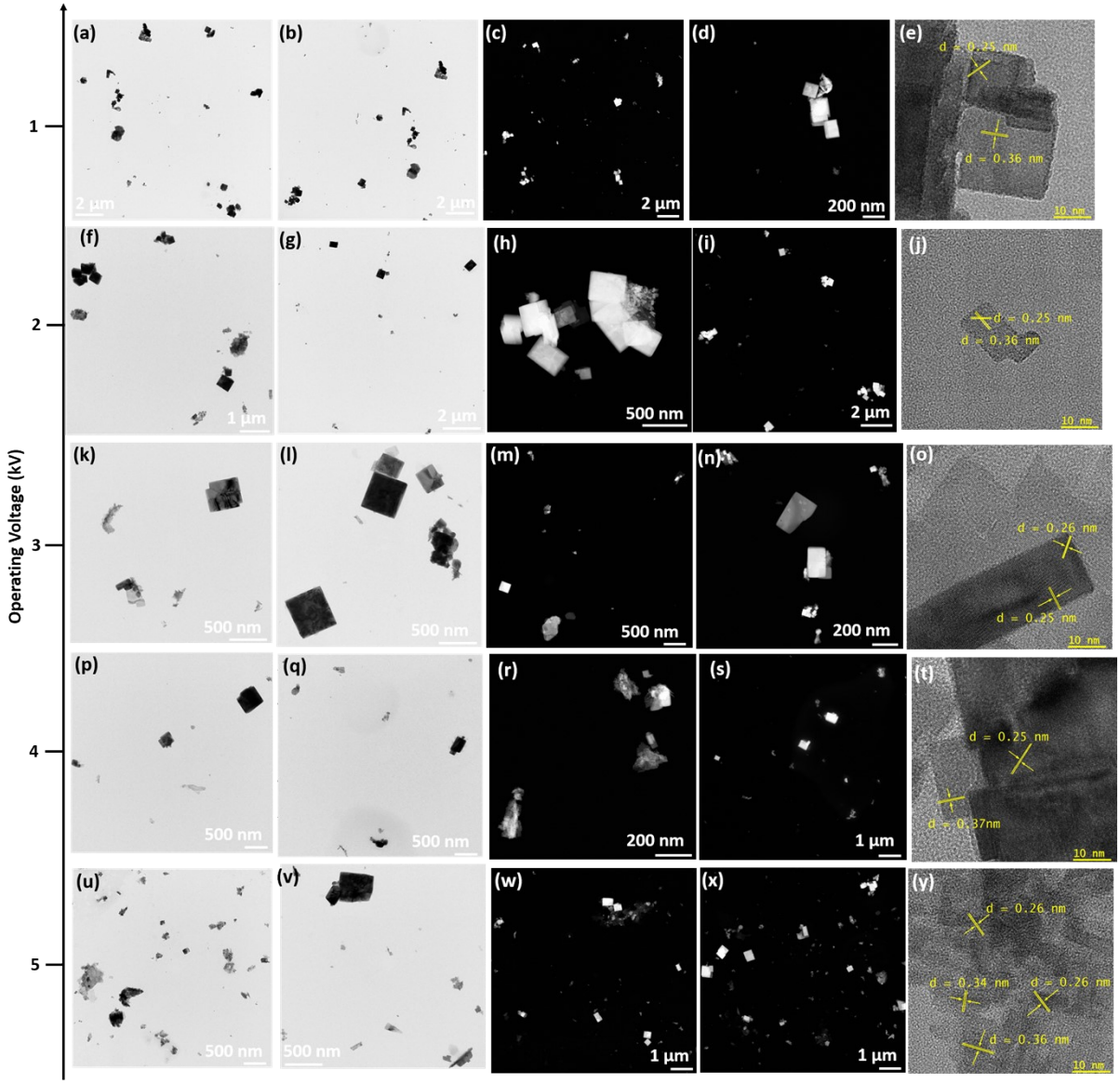



**Fig. S8.** Large area TEM (a, b, f, g, k, l, p, q, u, v), HAADF-STEM (c, d, h, i, m, n, r, s, w, x) and DigitalMicrograph processed HRTEM images (e, j, o, t, y) at the applied potential, V =1-5 kV and tip-to-substrate distance, L = 3 cm.

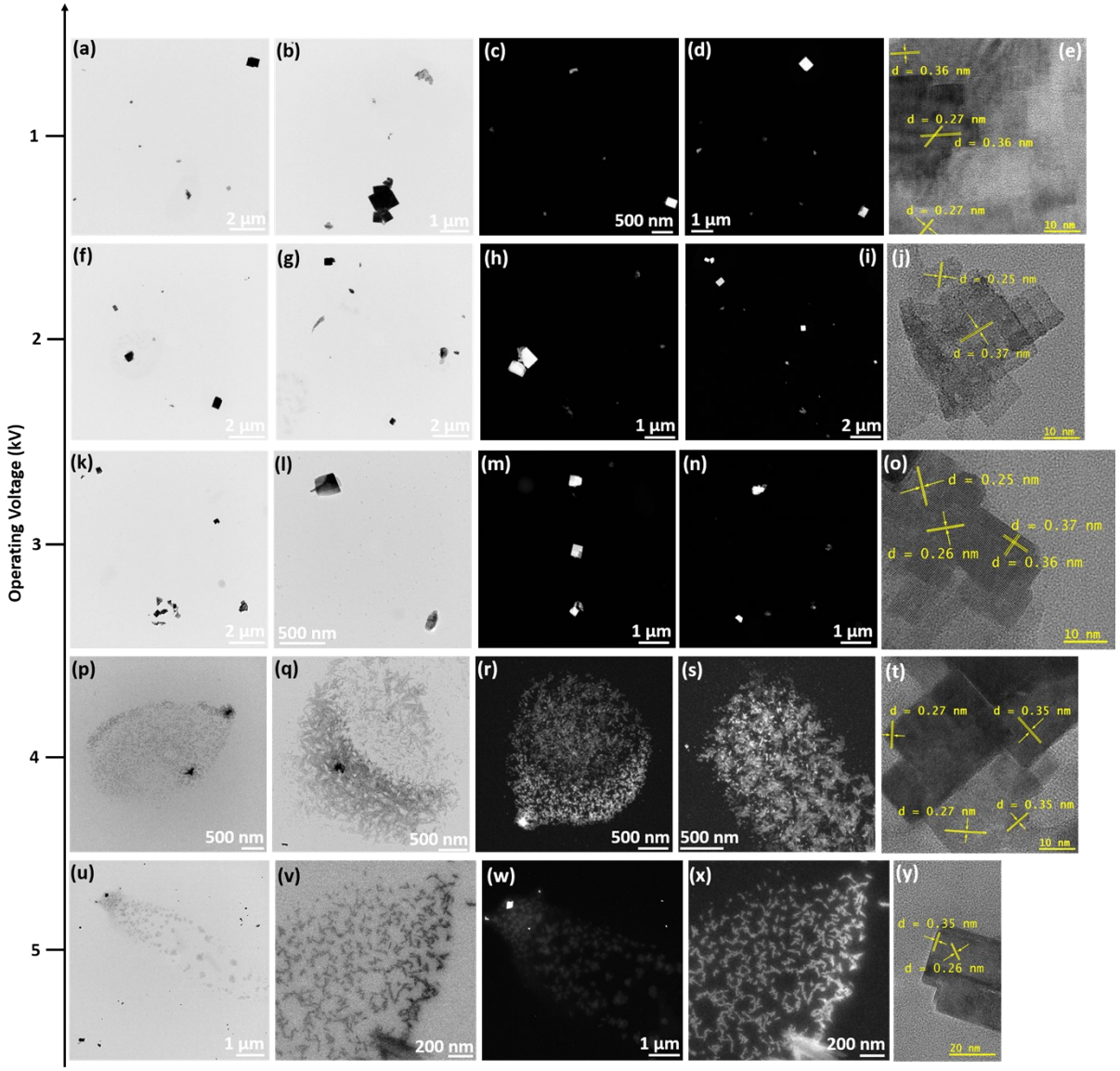



**Fig. S9.** Large area TEM (a, b, f, g, k, l, p, q, u, v), HAADF-STEM (c, d, h, i, m, n, r, s, w, x) and DigitalMicrograph processed HRTEM images (e, j, o, t, y) at the applied potential, V =1-5 kV and tip-to-substrate distance, L = 4 cm.

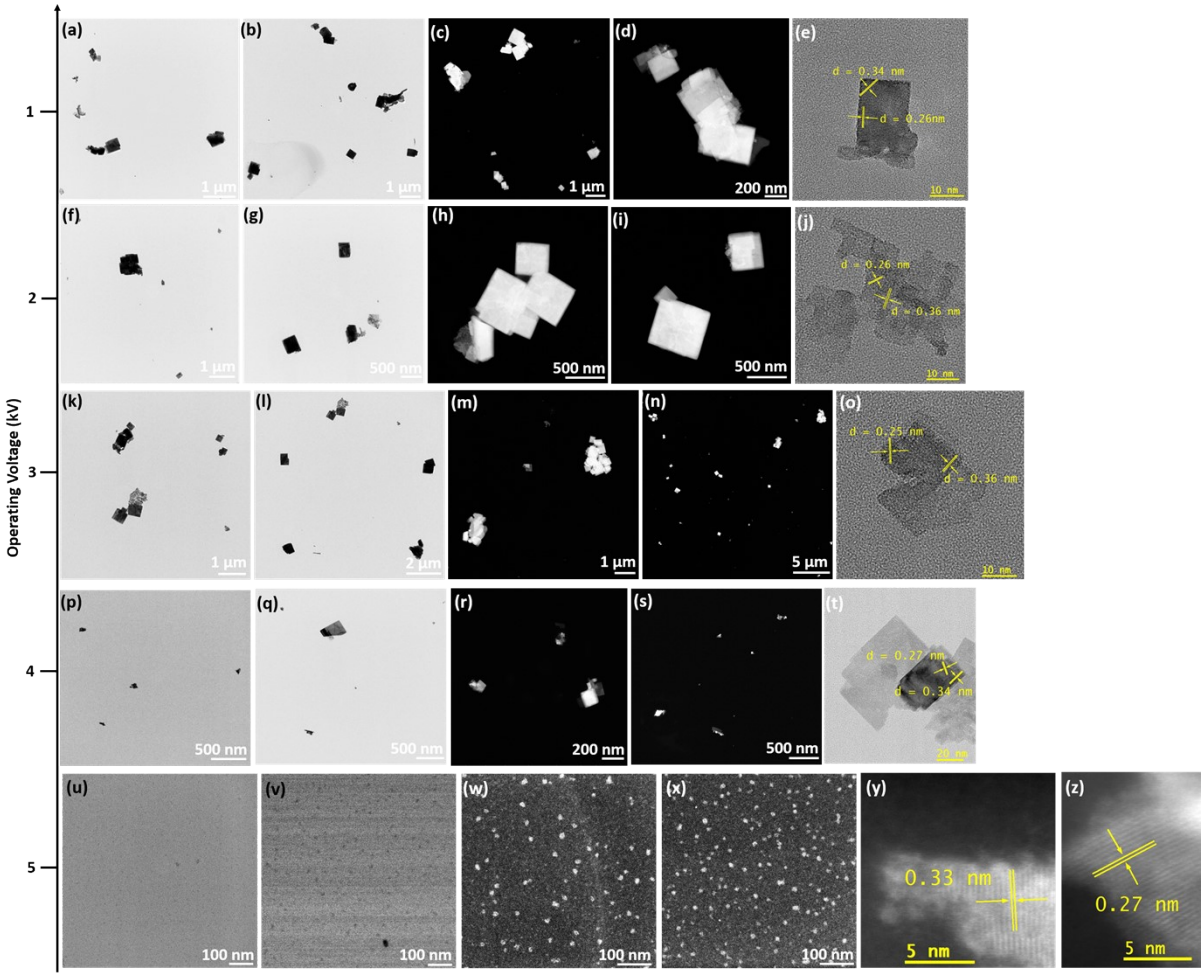



**Fig. S10.** Large area TEM (a, b, f, g, k, l, p, q, u, v), HAADF-STEM (c, d, h, i, m, n, r, s, w, x) and DigitalMicrograph processed HRTEM images (e, j, o, t, y, z) at the applied potential, V = 1-5 kV and tip-to-substrate distance, L = 5 cm.

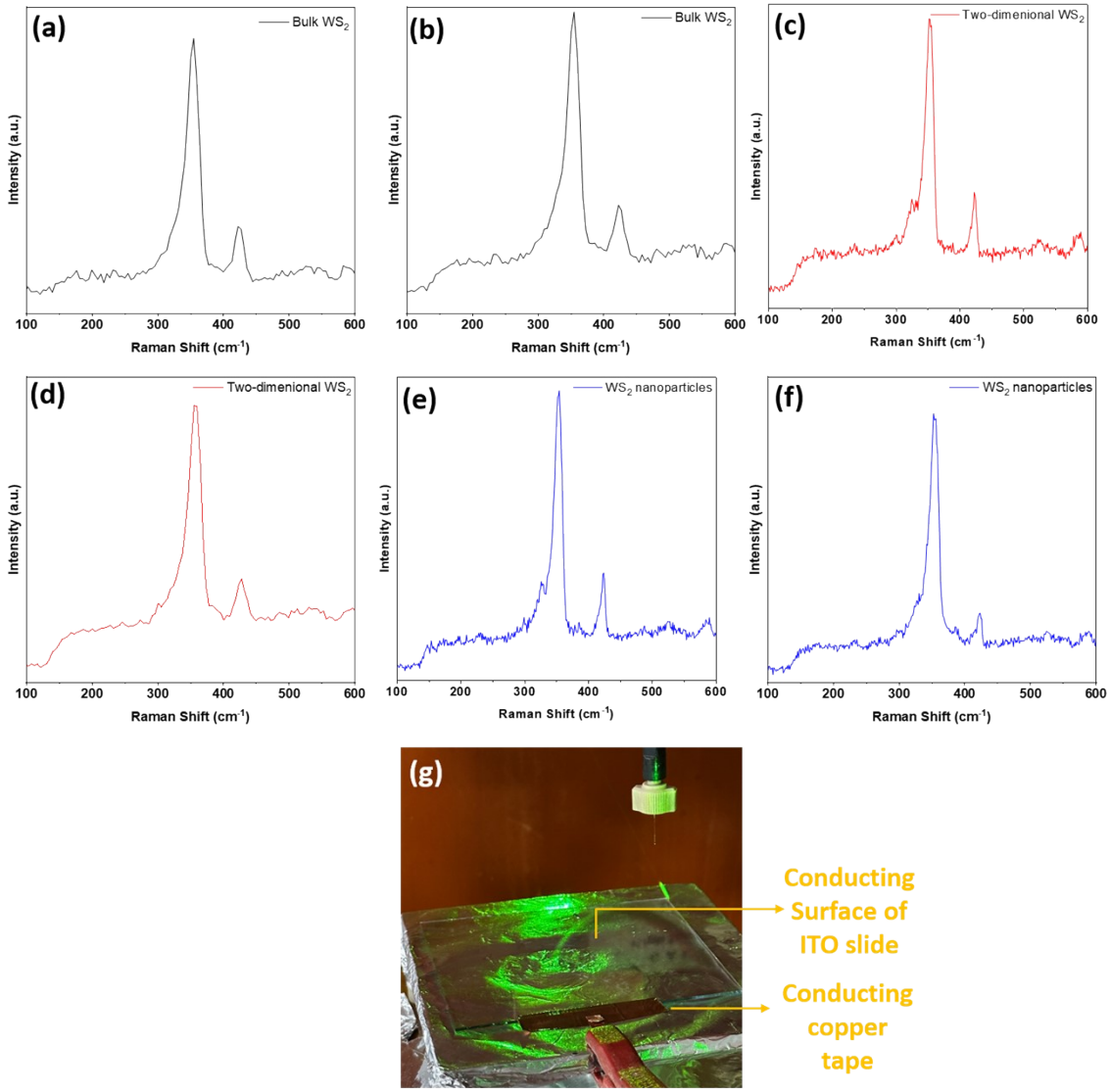



**Fig. S11.** Raman spectrum of Bulk $WS_2$ (a, b), two-dimensional $WS_2$ (before spray) (c, d), Raman spectrum of $WS_2$ nanoparticles (after spray) (e, f) obtained from different region. Photograph showing the different components of the home-built electrospray set-up used for collecting $WS_2$ nanoparticles for Raman analysis. An ITO glass slide was kept on the substrate below the tip of the capillary which is connected via conducting copper tape to grounding. The spray plume was visualized by a green laser (g).

## References

1 J. J. Métois and P. Müller, *Surf. Sci.*, 2004, **548**, 13–21.