

Particle

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Supporting Information

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Atomically Precise Transformations and Millimeter-Scale
Patterning of Nanoscale Assemblies by Ambient Electrospray
Deposition

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Experimental section

Materials:

All the chemicals were commercially available and were used without further purification. Tellurium dioxide (TeO₂, 99.9%) powder, hydrazine monohydrate (N₂H₄.H₂O, 99-100%) and PVP (Polyvinylpyrrolidone, K30) were supplied by Alfa Aesar, Fischer Scientific and SD Fine Chemicals, respectively. Ethylene glycol (LR) and sodium hydroxide (NaOH) pellets were procured from RANKEM, India. Anhydrous acetonitrile (HPLC grade) from Merk Specialities Private Limited, India, was used as solvent in all electrolytic spray experiments. Indium tin oxide-coated glass slides were obtained from Aldrich, India while copper TEM grids, used as masks, were purchased from Tedpella Inc. USA. Milipore water (18 kΩ) was used as solvent for electro spray depositions experiments.

Synthesis of Te NWs

Ultrathin Te NWs were synthesized by hydrothermal reduction of Te(IV) precursor with hydrazine hydrate. In this modification of a known synthetic strategy, 66.5 mg of TeO₂ was dissolved in 2mL 2M NaOH solution. This solution was mixed with a polyvinylpyrrolidone

(PVP) solution containing 500 mg of PVP (K30) in 30 mL of distilled water in a Teflon-lined stainless steel autoclave. To this 2.5 mL of 25% aqueous ammonia solution was added dropwise under constant magnetic stirring followed by the injection of 500 μ L of 99% $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. The mixture was further stirred for 15 min and then was maintained at 180 °C for 3 h. Formation of a dark blue colored suspension indicated the formation of Te NWs which was subsequently confirmed by optical absorption spectroscopy and transmission electron microscopy (tens of micron long wires of ~8 nm diameter).

Freestanding aligned monolayer of Te NWs

Aligning the NWs in the form of a monolayer assembly involve two steps. In the first step, ultrathin Te NWs were subjected to centrifugal precipitation and redispersion cycles to get rid of the excess PVP. 5 mL of the as synthesized NW dispersion was diluted and centrifuged at 15000 rpm for 15 min, twice with water and finally once with ethanol. The pellet obtained after the final centrifugation step was then dispersed in 2 mL of 1-butanol.

In the second step, NW dispersion in butanol was slowly added drop-wise on the surface of water from a pipette. A thin bluish film formed on the surface of water within a couple of minutes. This film was then transferred onto the TEM grids for examination with an electron microscope to confirm its identity as the monolayer assembly of the ultrathin Te NWs.

Electrolytic/electro spray deposition

NanoESI sources, used for generating the spray, were made in-house by pulling borosilicate glass capillaries having an inner diameter of and outer diameter of 0.86 and 1.5 mm, respectively on a micropipette puller. The capillaries were filled with anhydrous acetonitrile using micro-injector pipette tips for spray deposition. A silver wire (metal wire) of diameter ~0.5 mm was inserted inside the solvent filled spray emitters as the source of metal ions (in case of electrolytic spray) as well as the electrode. The wire was connected to a high voltage power source through a copper clip.

Optimized parameters for electrospray deposition are given in the table below:

Parameter	Optimized value
Electrospray voltage	1.5-2.5 kV (Varied to maintain a fixed ion current depending on the surface tension of the solvent used)
Diameter of nESI tip	15-20 μ m
Ion current	50-60 nA
Concentration of the precursor solution	10 mM
Flow rate of the solution	20 nL/min
Distance of the electrospray emitter from the surface	Approximately 10 mm

Duration of deposition was optimized in a trial and error basis for complete conversion of the Te NWs. In the case of Ag deposition, deposition-time as 2 h at an ion current of 50 nA.

Instrumentation

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed at an accelerating voltage of 200 kV on a JEOL 3010, 300 kV instrument equipped with a UHR polepiece. A Gatan 794 multiscan CCD camera was used for image acquisition. EDS spectra were collected on Oxford Semistem system housed on the TEM. NPs formation during electrolytic/electro spray deposition was directly examined on 300-mesh carbon coated copper grids (spi Supplies, 3530C-MB). Te NW assembly floating on water was transferred on the grids and dried in ambient condition, before TEM analysis. Chemical transformations of the NWs were probed on these grids after electrolytic/electro spray deposition of metal ions. Nano ESI sources used in the experiments were prepared in-house on a micropipette puller by Sutter instrument, USA. Mass spectra were collected using an ion trap LTQ XL (Thermo Scientific, San Jose, California) mass spectrometer. Raman spectra were recorded on a Witec alpha300 S confocal Raman spectrometer with a 633 nm (He-Ne) laser using a Zeiss 20x objective. Spectral data was processed by the Witec Project Plus software package.

Supporting information figures

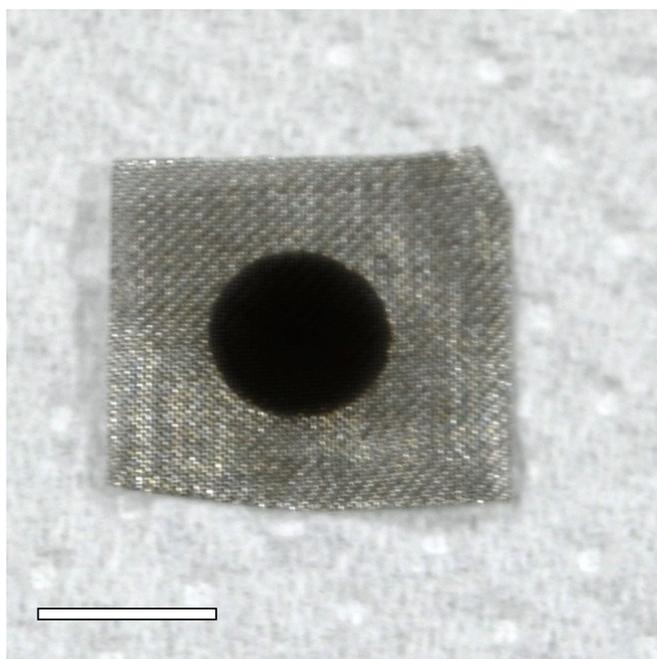


Figure S1. Photograph of electrolytically deposited silver NPs on an SS wire mesh. Scale bar is 3 mm.

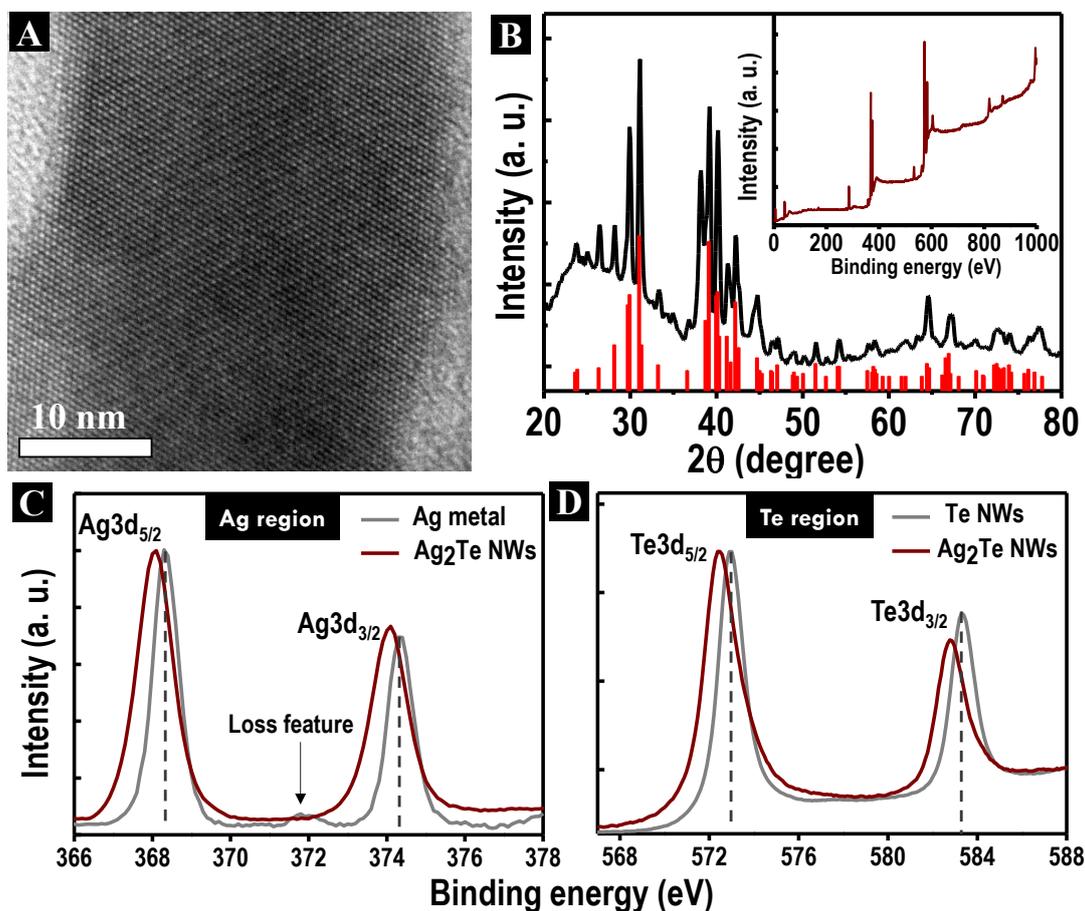


Figure S2. (A) HRTEM image of a transformed Ag_2Te NW showing its single-crystalline nature indicating uniform transformation across its whole volume. (B) XRD pattern of the transformed NWs, showing the formation of a single monoclinic phase of Ag_2Te . Corresponding JCPDS stick pattern [Card No. 34-0142] is also shown. XPS spectrum for the Ag_2Te NWs is shown in the inset. (C) XPS spectra of the Ag 3d region for the Ag_2Te NWs and metallic silver confirming the presence of Ag (I). (D) XPS spectra of the Te 3d region for the Ag_2Te NWs and Te NWs confirming the presence of telluride.

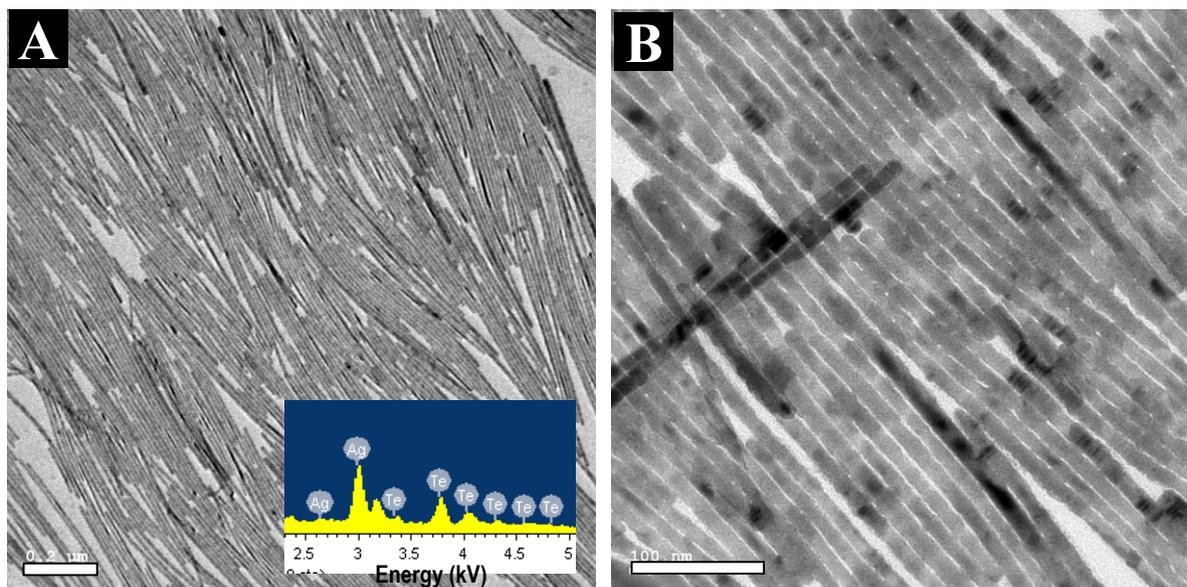


Figure S3. (A) Monolayer assembly of preformed Ag_2Te NWs made at the air-water interface. These NWs were prepared through solution phase reaction of Ag^+ ions with Te NWs. EDS spectrum shown in the inset confirms the NW composition. (B) A higher magnification TEM image of the same. Bending of NWs due to Te to Ag_2Te transformation observed for solid state transformation was not observed. Scale bar is 200 nm in image A and 100 nm in image B.

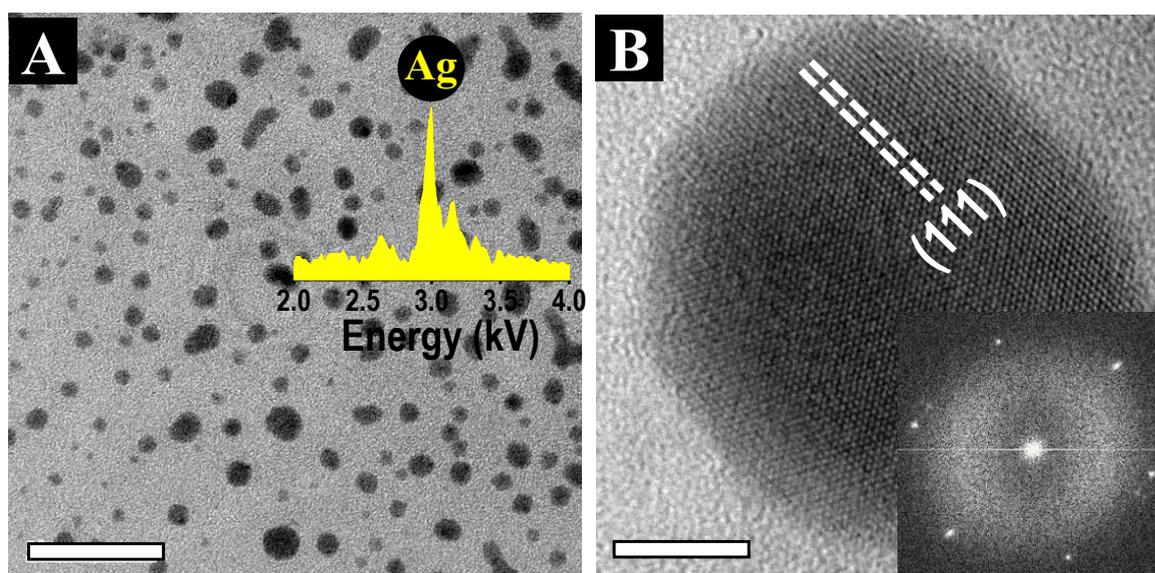


Figure S4. (A) TEM image of the Ag NPs formed on grounded TEM grid through electrolytic deposition of silver. EDS spectrum given in the inset shows the presence of only silver. (B) HRTEM image of one such Ag NP. Corresponding FFT pattern is shown in the inset. Lattice plane is marked. Scale bar is 50 nm in image A and 2 nm in image B.

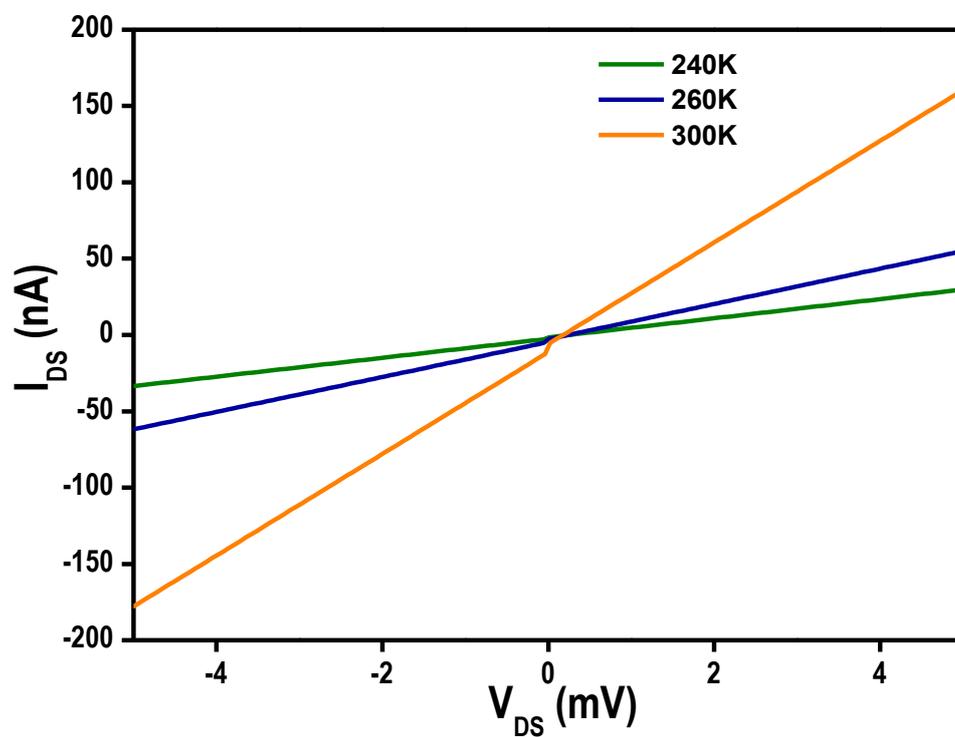


Figure S5. I-V curve for a monolayer of Te NWs.

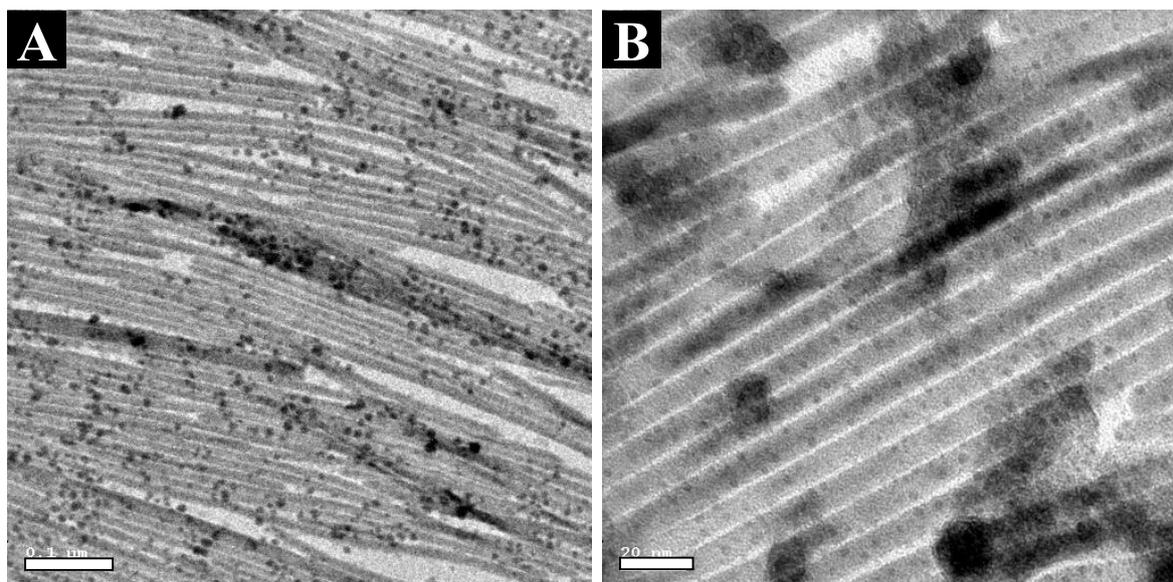


Figure S6. (A) TEM image showing formation of Ag nodules on Ag_2Te NWs upon electrolytic spray deposition of silver. (B) A higher magnification image. Scale bars are 100 and 20 nm for image A and B, respectively.

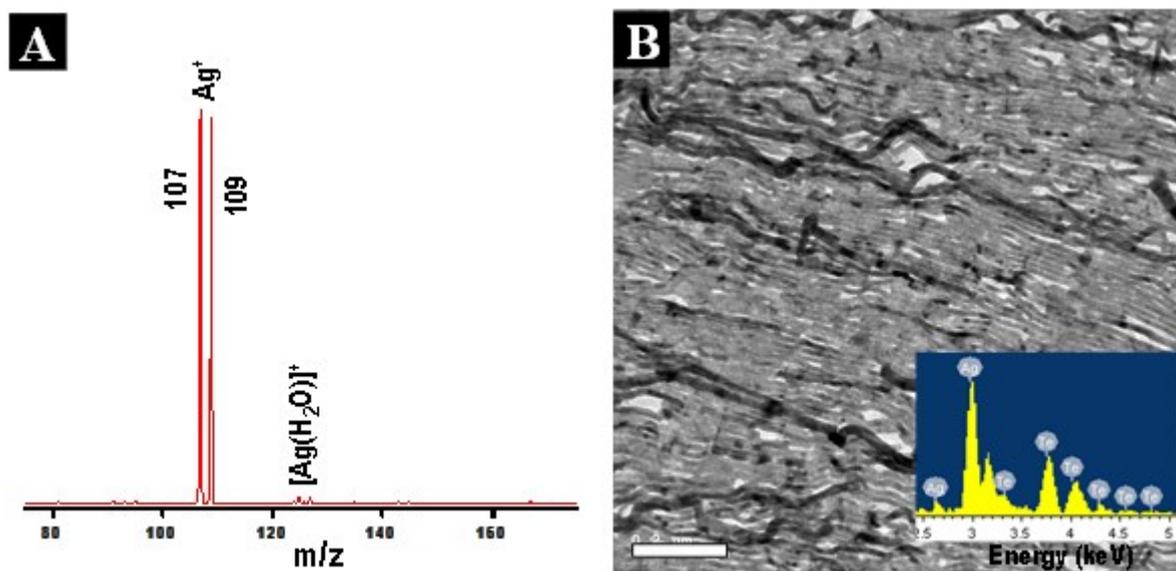


Figure S7. (A) ESI mass spectrum of an electrospayed aqueous solution of silver acetate showing presence of silver ions. (B) Monolayer of Ag₂Te NWs prepared by electrospaying silver acetate on a monolayer of Te NWs. The composition of the NWs was confirmed from EDS spectrum (shown in the inset). Scale bar in image B is 200 nm.