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<Supplementary information>

Ionic Strength Induced Electrodeposition: A Universal Approach for Nanomaterials Deposition at Selective Areas

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Methods

Materials: Copper grids (70 µm line width × 0.4 µm line thickness with 1 mm spacing, given as a gift from Hanita Coatings, Israel) were pre-formed on PET and cleaned with ethanol (99%, Merck) and deionized (DI) water for 10 min sonication prior to use. The copper plates (25 mm length × 10 mm width × 0.5 mm thickness) served as the electrodes and substrates for VO_2-NP deposits, which were used for immersing in HCl. The plates were first polished with a 6 µm diamond suspension (Buehler, USA) and cleaned by sequentially sonicating in ethanol, acetone (Gadot, Israel) and DI water for 20 min, followed by Ar plasma cleaning (Diener Electronic, Germany) each side for 10 min. VO_2-NP (99.9%) were purchased from JingCheng Chemicals, China, and dispersed homogeneously in different concentrations (0.5/0.75/1.0 wt%) in DI water by ultra-sonication at 55 °C for 30 min. The AuNP (6-7 nm diameter, 63.2 µg mL^{-1}) dispersion in water with citric acid as stabilizer was purchased from British Biocell, UK. The MWCNT (10-20 nm thickness, 0.5-2 µm length) were obtained from Cheap Tubes Incorporation (USA). The 0.5 wt% MWCNT were dispersed in a mixture of 1 wt% cetyltrimethylammonium bromide (CTAB), 25 vol.% N-methyl-2-pyrrolidone (NMP) and DI water prior to electrodeposition. The 0.1 mg mL^{-1} GO dispersion in DI water was purchased from GRAnPH, Spain. NH_4Cl, KCl, K_2SO_4, $CuCl_2$, H_2SO_4 and HCl (37%), were acquired from Sigma-Aldrich and used as purchased. DI water (18.3 MΩ cm^{-1}, EasyPure UV, Barnstead, UK) was used for all the experiments.

Electrodeposition: All electrodeposition experiments were performed with a CHI 750B potentiostat (CH Instruments, USA) at room temperature using a standard three-electrode setup with an Ag/AgBr wire as a quasi-reference electrode (QRE) and a Pt wire as a counter electrode. The working electrodes were the substrates, namely Cu grids on PET and Cu plates. A constant potential (which was varied between experiments) was applied to the working electrode for 20 to 180 s. After deposition, the films or grids were blow-dried with N_2 or Ar flow and the samples were placed in the vacuum desiccator overnight before characterization. The deposits thickness was investigated using a home-made Teflon O-ring electrochemical cell with a defined deposition area of 19.63 mm^2.

Additionally, the deposits were immersed in 0.01 mol L^{-1} HCl for 1 to 5 min with magnetic stirring for removing copper ions.

Adhesion test: The adhesion between the VO_2-NP deposits and substrate was evaluated by the use of a cross-cut tape test, following ASTM D 3359-09[1] using a 3M Scotch® # 600 transparent tape.[2-4] The VO_2-NP deposited on Cu plate was cross-cut into lattice pattern. The tape was pasted firmly over the lattice for 90 ± 30 s before removing rapidly at an angle close to 180 °. The tape tests were repeated 3 times at the same location by using a new area of the tape for each time. For reporting the adhesion strength, the calculation of the area affected was done by using Photoshop software CS version (Adobe System Inc., USA) according to the following equation (S1).

$$\mathit{Percent\ area\ removed} = \frac{\mathit{Pixels\ before\ applying\ the\ tape} - \mathit{Pixels\ after\ removing\ the\ tape}}{\mathit{Pixels\ before\ applying\ the\ tape}} \times 100\%$$

(S1)

Characterization: The ζ-potential and average particle size of VO_2-NP were measured using Zetasizer Nano-ZS DLS instrument (Malvern instruments, UK) at various pH values and ionic strengths. The pH was measured just prior to the ζ-potential measurement and the selected electrolytes were added (in various concentrations) to the 1 wt% VO_2-NP dispersion to achieve a series of ionic strengths. The ζ-potentials of 63.2 µg mL^{-1} AuNP and 0.05 wt% MWCNT were determined by the same instrument without altering the pH of solutions. The size and shape of nanomaterials were characterized by the extreme high resolution (XHR) SEM Magellan TM 400L (FEI, USA), which was equipped with an EDX detector (X-Max 20, Oxford Instruments, UK) for analyzing the composition before and after removing the copper ions. Characterization of AuNP and the elemental mapping of V and Cu were carried out using high resolution TEM Tecnai F20 G2 (FEI, USA) with EDX detector (X-Max 20; spectral resolution133 eV) and HAADF detector, allowing high resolution scanning transmission electron microscopy (STEM) Z-contrast imaging. XRD patterns within the 2θ range 10 ° to 60 ° were recorded on a D8 Advance diffractometer (Bruker AXS, Germany) at room temperature using CuKα radiation (λ=1.5418 Å). XPS analysis was performed with Kratos Axis Ultra spectrometer (Kratos Analytical Ltd., UK) using Al-Kα monochromatic radiation X-ray source (1486.7 eV) and the binding energies were calibrated using C 1s peak energy as 285.0 eV. Raman scattering was performed on the InVia Raman microscope (Renishaw plc, UK) using a 514 nm laser source. The thickness of the deposits was measured using a surface profilometer (P 15, KLA-Tencor Co., USA). The optical transmittance in the wavelength range of 250~2200 nm was recorded using the Lambda 1050 UV-Visible-Near IR spectrophotometer (UV-Vis-NIR, PerkinElmer, USA) with Peltier temperature control accessory.

The integrated luminous transmittance (T_{lum}, 380 nm-780 nm) and solar transmittance (T_{sol}, 280 nm-2200 nm) were calculated based on the measured transmittance spectra using the following expression (equation (S2)), while the corresponding energy modulation abilities were characterized as ΔT_{lum} and ΔT_{sol} (equation (S3)) as the contrast of the integrated transmittance at low (20 °C) and high (90 °C) temperature.

$$T_{lum/sol} = \frac{\int \Phi_{lum/sol}(\lambda) T(\lambda) d\lambda}{\int \Phi_{lum/sol}(\lambda) d\lambda}$$

(S2)

$$\Delta T_{lum/sol} = T_{lum/sol(low)} - T_{lum/sol(high)} \qquad \text{(S3)}$$

Where $T(\lambda)$ represents the measured spectral transmittance. Φ_{lum} is the standard luminous efficiency function of photonic vision,[5] and Φ_{sol} is the solar irradiance spectrum distribution for air mass 1.5[6] as it represents an overall yearly average for mid-latitudes including diffuse light from the ground and sky on a south facing surface tilted 37° from horizontal.

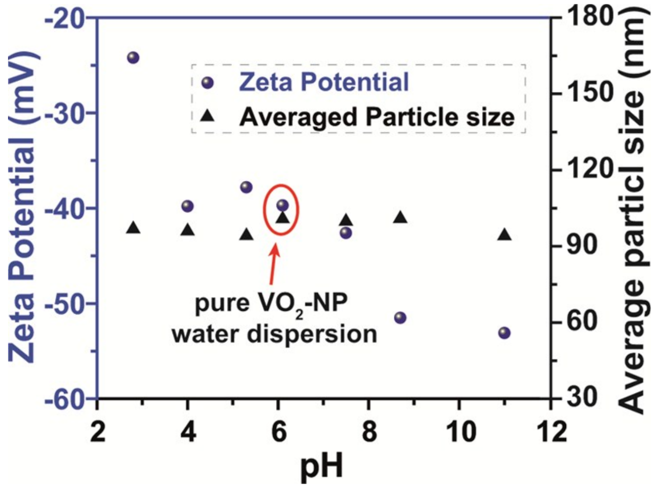


Figure S1| Effect of pH. DLS results show the effect of pH on the ζ-potential (blue spheres) and the average particle size (black triangles) of VO_2-NP.

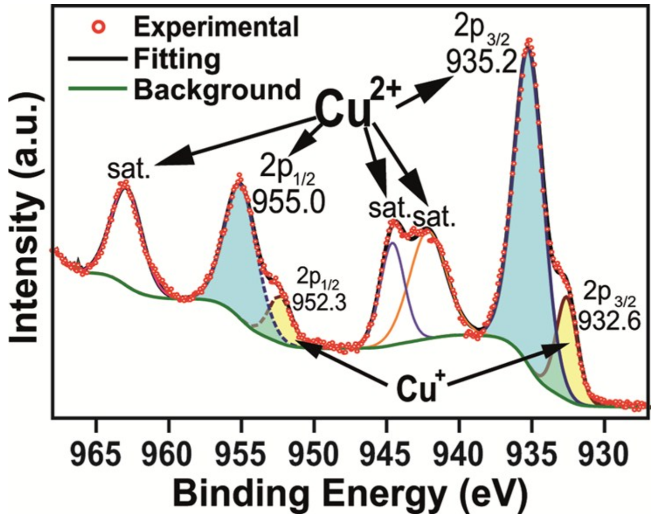


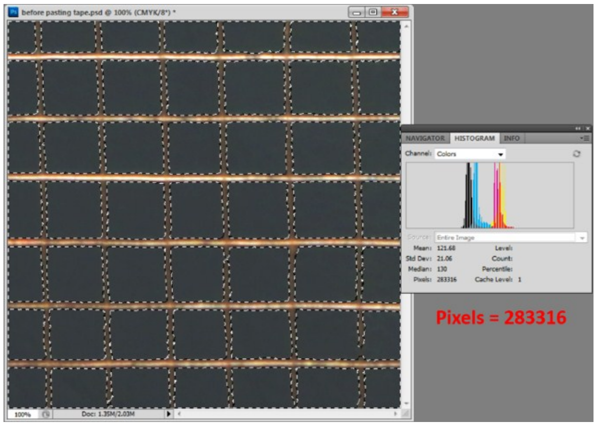
Figure S2| Presence of Cu ions in the VO_2-NP deposits. Cu 2p XPS peaks of the VO_2-NP deposited on Cu substrate at 0.1 V (vs. Ag/AgBr) for 45 s

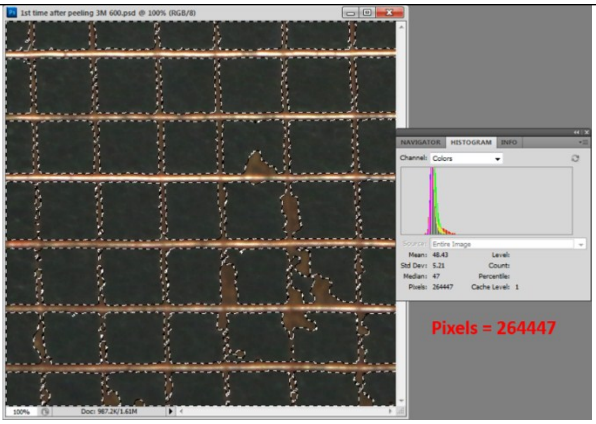
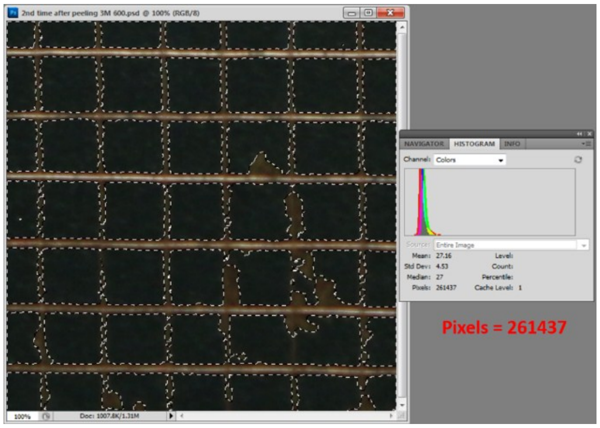
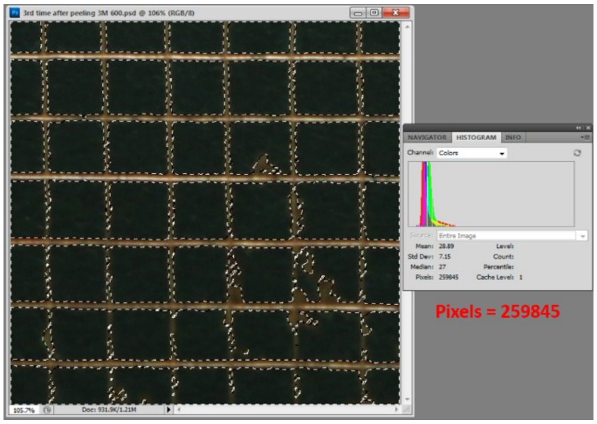
Table S1| Electrochemically generated c_i (average) of Cu^{2+} close to electrode surface under different electrodeposition conditions

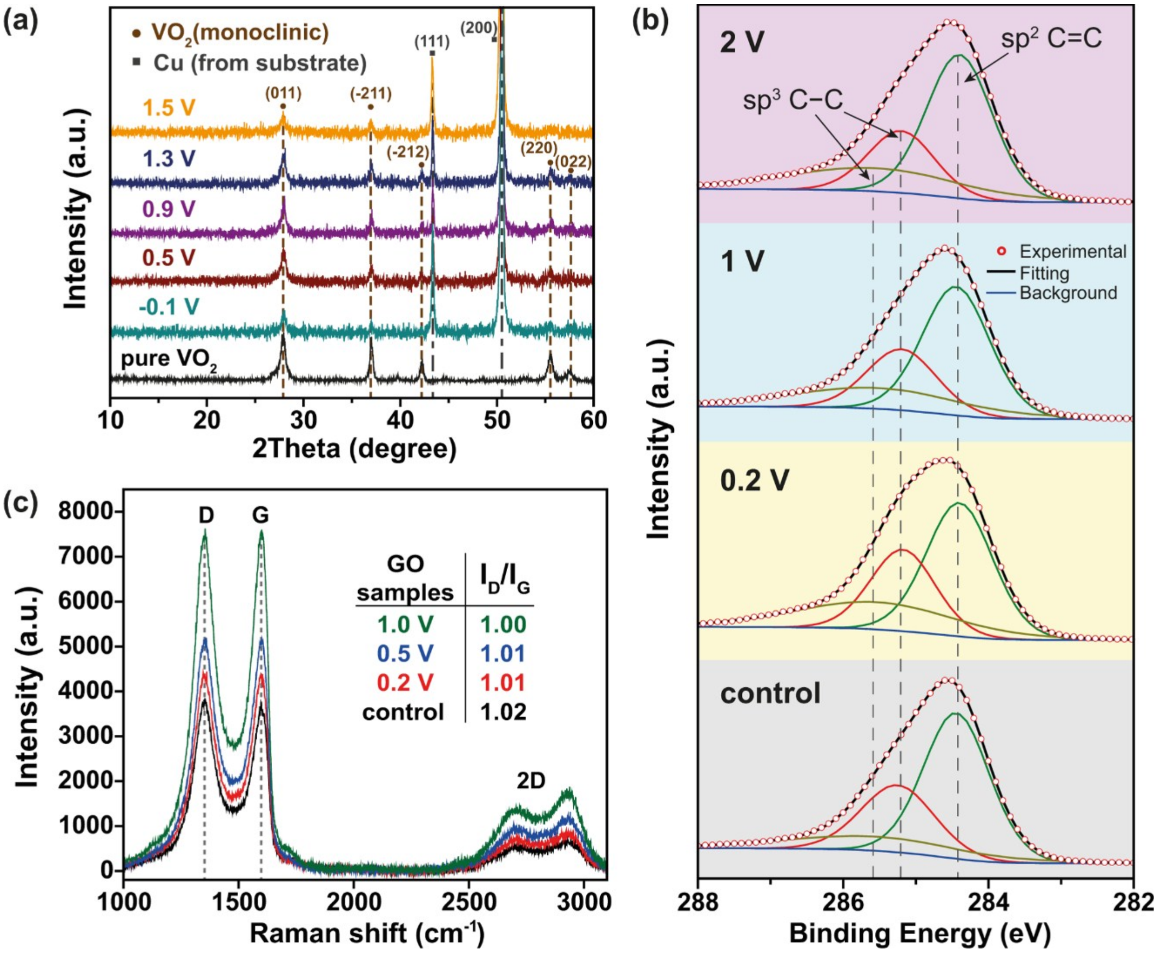
Deposition	*Potential (V)*	*Cumulative*	*Average c_i of Cu^{2+}*

time (s)	*(vs. Ag/AgBr)*	*charge (μC)*	*(mmol L^{-1})*
10	0.00	81	0.25
20	0.00	164	0.36
	0.05	180	0.40
	0.10	208	0.46
	0.15	234	0.52
	0.20	277	0.61
50	0.05	445	0.98
Ref.: CCC_{CuCl_2}	-	-	0.25

Table S2| Adhesion tests of VO_2-NP deposits on Cu substrates according to ASTM D 3359-09 Cross-Cut Tape Test

No. of ASTM D 3359-09 tape test	**Percent area removed**
Making the required cuts before applying the tape  before pasting tape.psd @ 100% (CMYK/8*) * Channel: Colors Source: Entire Image Mean: 121.68 Std Dev: 21.06 Median: 130 Pixels: 283316 Level: Count: Percentile: Cache Level: 1 100% Doc: 1.35M/2.03M 	Not applicable
After the **1st** time of removing 3M # 600 tape	6.7%

 1st time after peeling 3M 600.psd @ 100% (RGB/8) Channel: Colors Source: Entire Image Mean: 48.43 Std Dev: 5.21 Median: 47 Pixels: 264447 Level: Count: Percentile: Cache Level: 1 Pixels = 264447 100% Doc: 987.2K/1.61M 	
After the **2nd** time of removing 3M # 600 tape  2nd time after peeling 3M 600.psd @ 100% (RGB/8) Channel: Colors Source: Entire Image Mean: 27.16 Std Dev: 4.53 Median: 27 Pixels: 261437 Level: Count: Percentile: Cache Level: 1 Pixels = 261437 100% Doc: 1007.8K/1.31M 	7.7%
After the **3rd** time of removing 3M # 600 tape  3rd time after peeling 3M 600.psd @ 106% (RGB/8) Channel: Colors Source: Entire Image Mean: 28.89 Std Dev: 7.15 Median: 27 Pixels: 259845 Level: Count: Percentile: Cache Level: 1 Pixels = 259845 105.7% Doc: 931.9K/1.21M 	8.3%



GO samples	I_D/I_G
1.0 V	1.00
0.5 V	1.01
0.2 V	1.01
control	1.02

Figure S3| Characterizations of various nanomaterials deposition on the Cu substrates. (a) XRD patterns of VO$_2$-NP deposited under different potentials (−0.1-1.5 V) as comparing with the patterns of the commercial VO$_2$-NP (monoclinic); (b) C 1s XPS peaks of MWCNT deposited under different potential (0.2-2 V) as comparing with the peaks of the commercial MWCNT dispersion (dip coated); (c) Raman spectra of GO deposited under different potentials (0.2-1.0 V) as comparing with the commercial GO sample (dip coated). The inset table shows the corresponding intensity ratios between D and G bands.

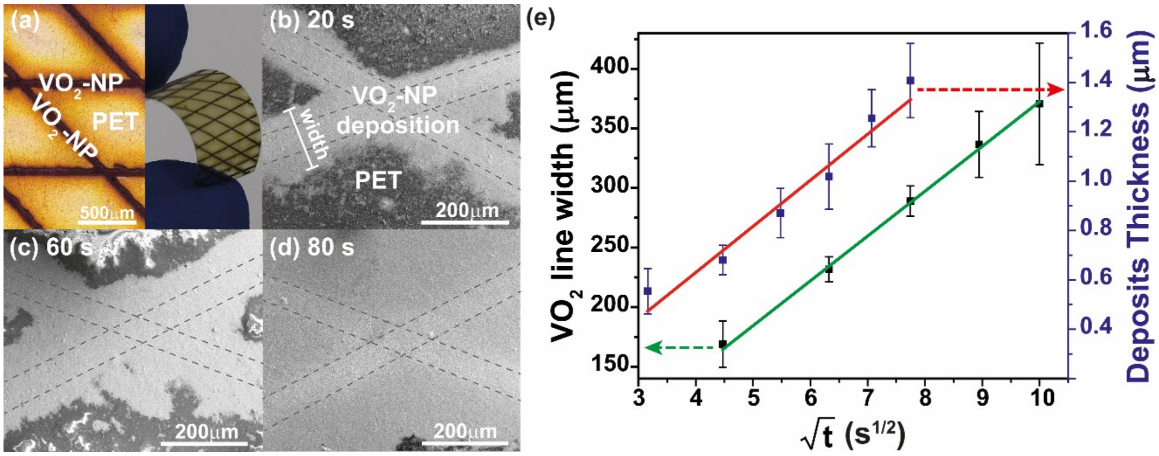


Figure S4| Depositions on flexible Cu grid substrates and the relationship between deposition time and the line width as well as thickness of VO_2-NP deposits. (a) Optical images for the 0.75 wt% VO_2-NP dispersion deposited on flexible Cu grid/PET substrate under 0.05 V (vs. Ag/AgBr) for 40 s. Notice that the grid is transparent. SEM images of the intersections on the grid deposited using 0.75 wt% dispersion under 0.05 V for (b) 20 s (dashed-line area reveals Cu grids beneath the deposit), (c) 60 s, (d) 80 s. Notice that the VO_2-NP deposit is brighter and the PET substrate is darker. (e) Line width (deposited 0.75 wt% dispersion) and deposits thickness (excluding the height of Cu line and using 1 wt% dispersion) as a function of the square root of deposition time.

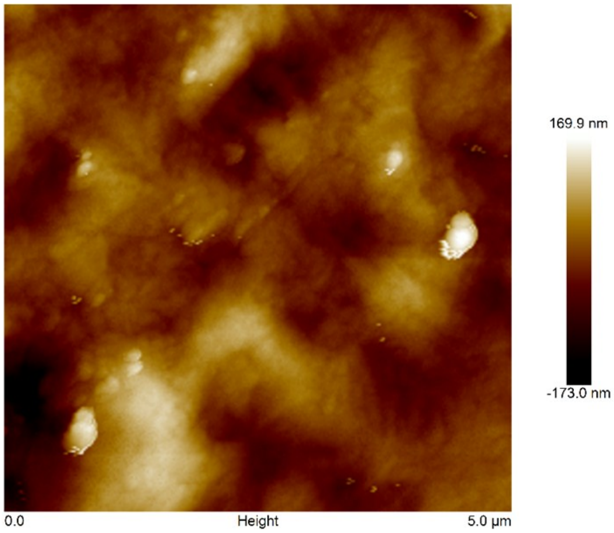


Figure S5| Surface roughness of Cu grids. AFM analysis scans a 5 μm × 5 μm area on the Cu line to demonstrate the topography of the electrode.

References:

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