

# In situ interfacial nanoengineering of imidazole-bridged one-dimensional $\text{AgVO}_3$ nanoribbons by Ag fractals

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1           **In-Situ Interfacial Nanoengineering of Imidazole Bridged-1D AgVO<sub>3</sub>**  
2                                   **Nanoribbons by Ag fractals**

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12

13 **Abstract**

14 The major bottleneck in harnessing the potential of solid-solid interfacial heterostructures  
15 involves incoherent interface constructions and complicated synthesis approaches. In this  
16 context, a synthesis strategy involving in-situ interfacial manipulation of imidazole bridge  
17 one dimensional (1D) single-crystalline nanoribbons is developed through dynamic growth  
18 of Ag fractals. This manuscript successfully demonstrates structural and morphological  
19 changes on the monoclinic patterns of silver vanadate nanoribbons with Wulff constructions.  
20 These are associated with in-situ electron beam perturbations and attributed to  $\beta$ -phase silver  
21 vanadate crystals. The dynamics and topological modifications induced on the nanohybrid  
22 interfaces mechanistically suggests the ability of the novel hybrid interfaces in harnessing and  
23 storing photogenerated auxiliary charge carriers. The synthesis methodology used enables in  
24 overcoming major bottleneck in nanoengineering of solid-solid interfacial heterostructures by  
25 utilizing real-time feedback of the imaging e-beam to precisely fabricate these  
26 heterostructures and study the interface transition.

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## 32 **Introduction**

33           Synthesizing exotic 1D hybrid interfaces with noble metal nanoparticles as surface-  
34 active sites is an attractive concept, but challenging (1-3). Blending metallic silver  
35 nanoparticles in vanadium oxide nano frameworks as an ultimate material has attracted  
36 considerable attention promising a broad spectrum of synergistic and integral characteristics.  
37 These are anticipated to find potential applications in energy storage, catalyst supports for  
38 surface-enhanced Raman spectroscopy, sensors, and biomedical devices, to name a few (4-  
39 8).Synthesis of such hybrid interfaces is however is an ardent task for which no traditional  
40 solution exists (9).Various synthesis approaches have been explored to synthesize such  
41 hybrid interfaces on  $\text{Ag}_2\text{WO}_4$ ,  $\text{Ag}_3\text{PO}_4$  and  $\text{Ag}_2\text{CrO}_4$  and  $\beta\text{-AgVO}_3$ (10-15), unfortunately  
42 lacks dynamic and tight control of fractal interfaces. Thus, exploration of unconventional  
43 synthesis method needs to be explored. Electron beam-based methods provide tight control of  
44 atomic arrangement. The e-beam mediated synthesis of interfacial morphologies plays a  
45 crucial role in tuning the characteristics of the core surfaces. Using electron beam source in  
46 imaging devices such as scanning and tunnelling electron microscopes provide real time  
47 dynamic control in nanofabrication of heterostructures. In this perspective a simple approach  
48 of using imaging electron beam, available in electron microscopes, to drive materials  
49 chemistry at nanoscale is rapidly growing.

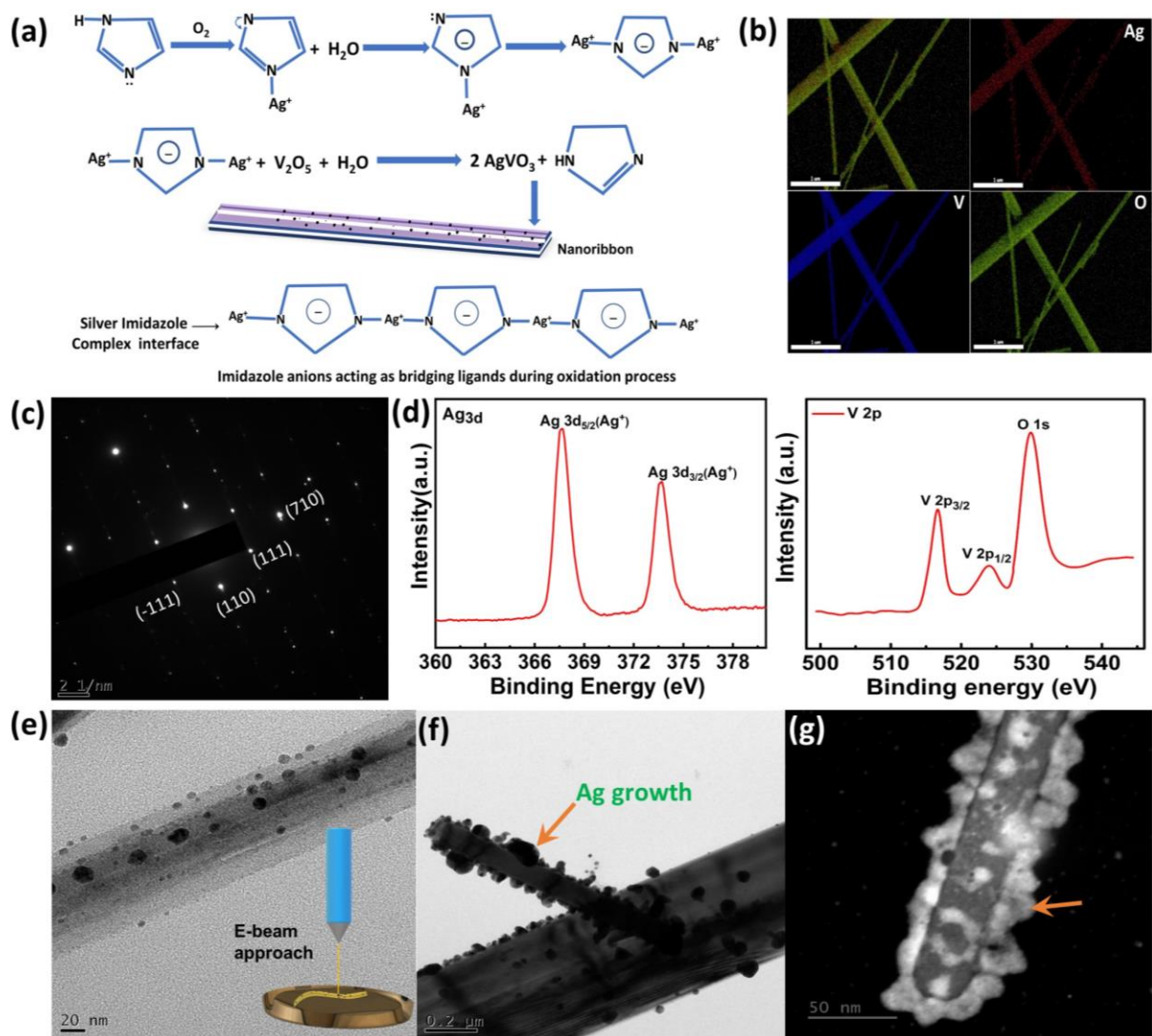
50           Here we have synthesized 1D  $\beta\text{-AgVO}_3$ nanoribbons by imidazole complexation as  
51 solid precursors to tailor surface engineering process, using imaging e-beam under high  
52 vacuum. The specimen is restructured into a hetero-structure fractal interface through in-situ  
53 nucleation and monitoring the growth of silver nanostructures when exposed to e-beam  
54 irradiation. The dynamic process involves generation of localized serrations, which are  
55 governed by the rate of the generated and annihilated defects/dislocations. Probing the  
56 dynamics and topography of the surface and interfaces revealed that the growth of metallic

57 Ag nanoparticles on semiconducting interfaces results in the cleavage of the electron-hole  
58 pair with increasing separation and the SPR effect would amplify the light absorption  
59 capacity (17). The charge transfer interactions induced due to SPR effect uncovers the  
60 immense potential of the heterostructure in electrochemical energy storage applications as  
61 well. This synthesis methodology enabled in nanoengineering of solid-solid interfacial  
62 heterostructures of Ag/AgVO<sub>3</sub> interface along with real-time feedback of the imaging e-beam  
63 to precisely fabricate these heterostructures and study the interface transition.

## 64 **Results and discussion**

65 The synthesis mechanism is shown in Figure 1(a). Imidazole, when dissolved in the solvent,  
66 its unprotonated molecule acts as ligand through the unshared pair of electrons on pyridinic  
67 nitrogen. The pyridinic nitrogen acts as a ligand site due to large electronegativity. Hence,  
68 complex formation is conceivable by ligation with metallic ions (18). Subsequently, the metal  
69 (silver) imidazolate complex formation occurs during the oxidation process. Conversely, a  
70 silver cation co-ordinate with one more nitrogen ligand. During the chemical reaction, the  
71 imidazole anions act as bridging ligands to co-ordinate with silver cations resulting in  
72 formation of complex bridging chain (19). When sufficient energy is supplied, the chain  
73 breaks and growth of heterostructure is initiated.

74 The elemental maps in Figure 1(b) shows the homogeneous distribution of Ag, V, and  
75 O over the surface of the nanoribbon before the growth. The selected area diffraction (SAED)  
76 pattern obtained from the nanoribbon shown in Figure 1(c) was indexed to the crystal lattice  
77 planes of  $\beta$ -AgVO<sub>3</sub>(Supporting information, Figure S1). The SAED spots reveal single-  
78 crystalline nature of the nanoribbons with diffraction planes assigned to (110), (-111), (111)  
79 and (710) of  $\beta$ -AgVO<sub>3</sub>.



80

81 **Figure 1.**(a) Schematic showing reaction mechanism and the growth of  $\beta$ -AgVO<sub>3</sub> ribbons.(b)  
 82 EnergydispersiveX-ray spectroscopy(EDS)elemental maps of the  $\beta$ -AgVO<sub>3</sub> ribbons. (c) SAED  
 83 pattern of  $\beta$ -AgVO<sub>3</sub> nanoribbon indexed to corresponding lattice planes. (d)XPS spectra of  $\beta$ -  
 84 AgVO<sub>3</sub> with high resolution peaks obtained for Ag 3d, V 2p and O 1s spectra respectively.(e)  
 85 TEM micrograph showing the effect of electron beam interaction with the nanoribbon and in-  
 86 situ grown Ag nanoparticles, (f)&(g) TEM and STEM micrographs showing the growth of  
 87 nanofractals respectively.

88 To understanding the chemical structure, purity, and valance states of the  $\beta$ -AgVO<sub>3</sub> ribbons  
 89 X-ray photoelectron spectroscopy (XPS) spectra was obtained and shown in Figure 1(d).  
 90 High-resolution XPS spectra obtained for the elements Ag, V and O have binding energies  
 91 corrected for charge offset by referencing C1s peak from surface adsorbed carbon at 284.8  
 92 eV. The hyperfine splitting of V2p core levels results in the photoemission at 516.6 eV and

93 524.2 eV. Single core level emission at 529.8 eV corresponding to O1s is observed. The  
94 high-resolution spectra of Ag 3d shows two firm Ag<sup>+</sup> peaks at 367.3 eV and 373.5 eV  
95 corresponding to Ag 3d<sub>(5/2)</sub> and Ag 3d<sub>(3/2)</sub>. The restructuring and growth phenomenon under  
96 the influence of an electron beam over a 1D AgVO<sub>3</sub> nanostructure support specimen is  
97 demonstrated in the study. Surface restructured process over crystalline nanoribbon is shown  
98 in Figure 1(e)-inset (A schematic illustration of e-beam process is shown; and for reference  
99 the morphology of pristine nanoribbons without Ag is shown in supporting Figure S2). The  
100 solid support specimen has multiple spots of contact with the conductive grid which assists in  
101 eliminating both thermal spikes and charging effects. The beam restructures the nanoribbon  
102 by channelling electronic energy to the targeted location. At sufficient energy, the beam  
103 ionizes the inner shell (20).

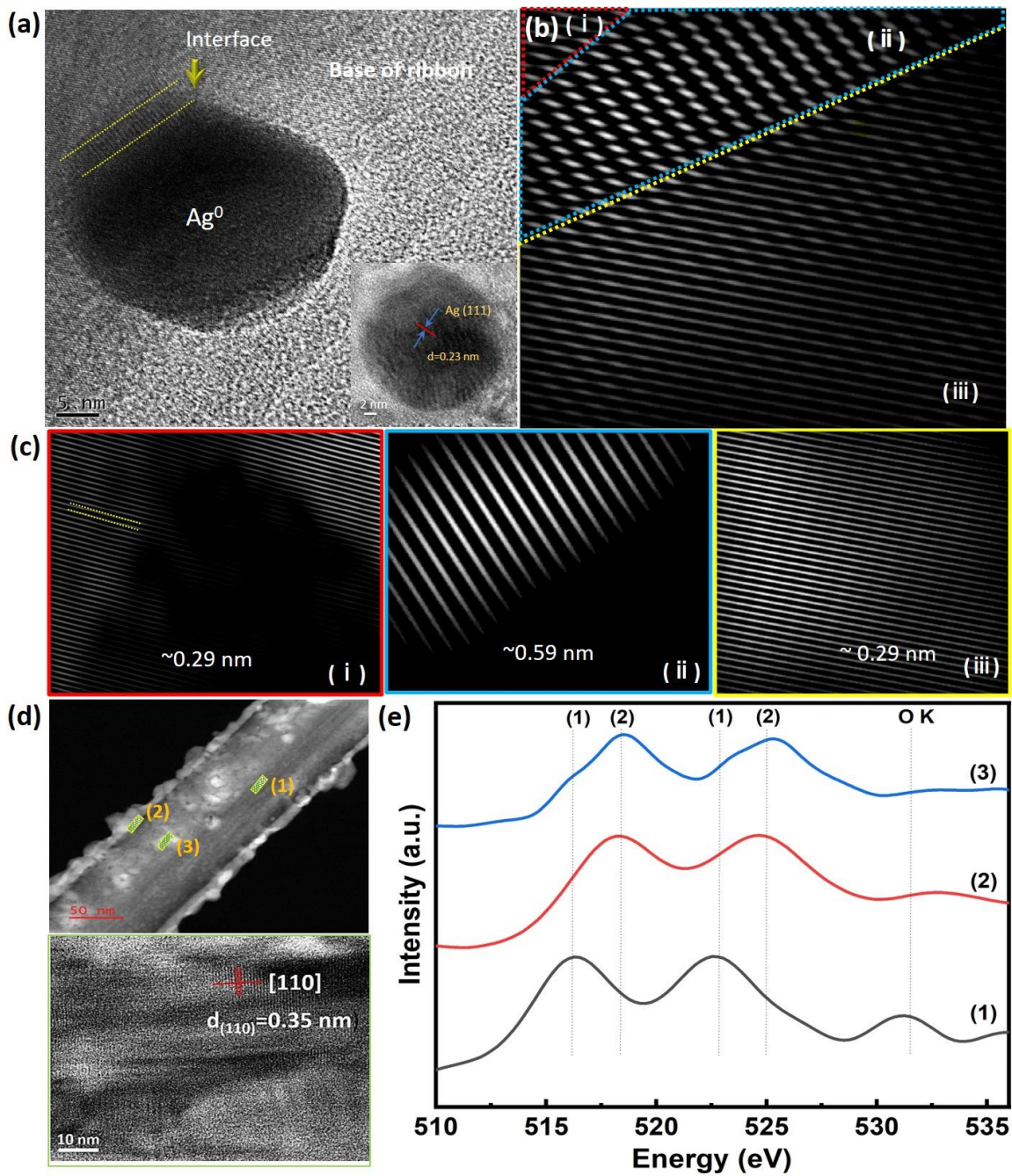
104 The energetic distribution of electrons over the bulk/surface induces electron-solid  
105 interactions (21). The electron trap-mediated reduction route drives the initial segregation of  
106 Ag nanoparticles. The TEM allows for examining the electron beam's role in Ag segregation  
107 trails by initial stages of nucleation followed by the growth of fractals. Exposure to a  
108 relatively low intense incident electron beam with a dose rate of 2.0-20.0 e Å<sup>-2</sup> s<sup>-1</sup> allows us  
109 to create a small cluster of Ag nanoparticles (2-5nm), as shown in Fig 1(e). From such  
110 considerations, as a function of electron beam illumination parameters, we can predict that  
111 through electron trapping, especially at the local defect sites, reduction of the Ag<sup>+</sup> to Ag<sup>0</sup> is  
112 initiated. During this early stage of the electron bombardment process, the beam stimulates  
113 charging effects with incongruent dissipation of thermal energy over the core to create local  
114 defects. These defects create hot spots for the accumulation of electrons inducing Coulombic  
115 forces (22). The electrostatic field then mobilises the ionised Ag nanoparticles, which were  
116 fragmented from the bonded Ag clusters. More incident electrons passing through interaction  
117 volume for a more considerable dwell time result in added ionization scattering events per

118 scan (For additional information, see Fig. S6), which would be adequate for surplus growth  
119 of Ag particles with diameters of about 10 nm (See Fig S5 (b), (d) and (f)) (23,  
120 24). Subsequently, as a function of time with an increase in cumulative electron dose (electron  
121 dose rates in the range of  $\sim 60\text{-}100\text{e } \text{\AA}^{-2} \text{ s}^{-1}$ ), the onset of coalescing Ag nanoparticles  
122 transcends at the nucleation edges. Random progression of Ag coalesces and diffusion-driven  
123 phenomenon under high beam currents resulted in Ag fractal growth (50-100nm) with  
124 structural transitions, as shown in Fig 1(f). The temperature gradient further drives  
125 nucleation outwards the nanoribbon surface. Hence the growth of the Ag fractals is preferably  
126 oriented along the edges of the support in lateral dimensions.

127 In scanning transmission electron microscopic (STEM) mode, a high angle annular dark-field  
128 (HAADF) image was acquired to ensure that only electrons deflected by larger angles were  
129 collected. Here we elucidated the effects on the sample support using the standard STEM  
130 approach of scanning the image sequentially. The STEM probe is held on each pixel in the  
131 micrograph, defining how fast the electron beam is rastered across the sample. Generally,  
132 STEM imaging will cause more severe electron induction than regular TEM mode operation  
133 damaging the specimen, and large beam currents may also induce sublimation effects (25).  
134 For comparison, HAADF- STEM imaging was also carried out in cryo-mode and assessed  
135 with HAADF-STEM images under ambient temperature conditions, as shown in supporting  
136 Fig. S9. The micrograph shown in Fig. S9 (b) has an apparent beam damage effect on the  
137 sample surface during prolonged exposure to the sample during STEM image data acquisition  
138 under ambient conditions. STEM data collected in cryo-mode (Fig. S9 (c)) using  
139 cryogenically cooled specimen offered low electron induction, which mitigated thermal  
140 decompositions to reduce the Joule heating effect and thermal diffusion (Details of the  
141 cryogenic cooling experiment is provided under the methods section and represented using a  
142 schematic in supporting information of Fig. S9. As shown in Fig S9 (d), a corresponding



143 EELS spectrum was also obtained. Thus, when STEM beam parameters are accommodated  
144 below a critical threshold, it will help us understand the growth dynamics under ambient  
145 temperature conditions. Hence fast scanning approach or changing the pixel dwell time  
146 during image acquisition is applied for low electron fluence. The incident electron beam was  
147 used as the STEM imaging probe and the ionising radiation source to stimulate growth by  
148 electron beam reduction. The actual exposure also relies on the time devoured in  
149 accumulating the data. Hence room temperature STEM mode image was obtained from a  
150 specific area within a controlled time, allowing us to evaluate the structural transition as a  
151 function of the total electron dose. From Fig 1(g), the scatter to high angles in the base region  
152 of the nanoribbon support decreased due to increased lattice disorder, and these regions have  
153 reduced intensity which displays reduction. Thus, under higher dose rates, the contrast  
154 variation spread is noticed from the base to the support edges. An additional contrast  
155 transition was observed at the periphery, associated with vacancy ordering and forming Ag  
156 fractals. From these observations, it appears that the beam current is analogous to the  
157 concentration of reducing agents for the growth of nanoparticles. Accordingly, the in-situ  
158 electron beam ionization of nanoribbon surface suggests that diffusion assisted process  
159 favours the growth of Ag fractals. Consequently, the transformation of Ag fractals to  
160 dendritic structures along the surface manifests the predominance of anisotropy over random  
161 progression of Ag aggregates. Thus, the segregation of the Ag nanoparticles provides high  
162 local charge densities and alter the surface potential (26). For a clear conception of the lattice  
163 defects that bend over the lattice planes, the incident beam is tilted just off Bragg's condition  
164 providing high resolution, mass-dependent low noise images. The surrounding matrix with  
165 densely accumulated charges renders the nanoparticles to interface with the nanoribbon  
166 support. The interfacial confinement of these metal nanostructures on the surface of the  
167 semiconducting nanoribbons



168

169 **Figure 2.** (a) Ag/AgVO<sub>3</sub> interface (b) interplanar spacings of segmented section of interface,  
 170 (c) IFFT images showing interplanar spacings with the section (i), (ii) and (iii), (d) EELS  
 171 micrograph (HAADF image) acquired at three different locations of nanoribbon with inset  
 172 (bottom) showing interplanar spacing of the nanoribbon and (e) EELS spectra showing  
 173 contributions of VL and OK obtained at the desired regions.

174

175 helps to passivate the surface defects and achieve better interfacial properties. The  
 176 phenomenon is anticipated to be supported by electron charge redistribution in the

177 nanoribbons due to electronic excitations coupled with the generation of silver vacancies  
178 (27). The excess electrons during the direct electron-beam irradiation can stimulate electronic  
179 and structural modifications in  $\beta$ -AgVO<sub>3</sub> crystals. The structural stability disturbed by  
180 interaction of electrons results in the phase transformation and in the formation of oxygen (O)  
181 and Ag vacancies. The following equation describes the growth process of Ag:

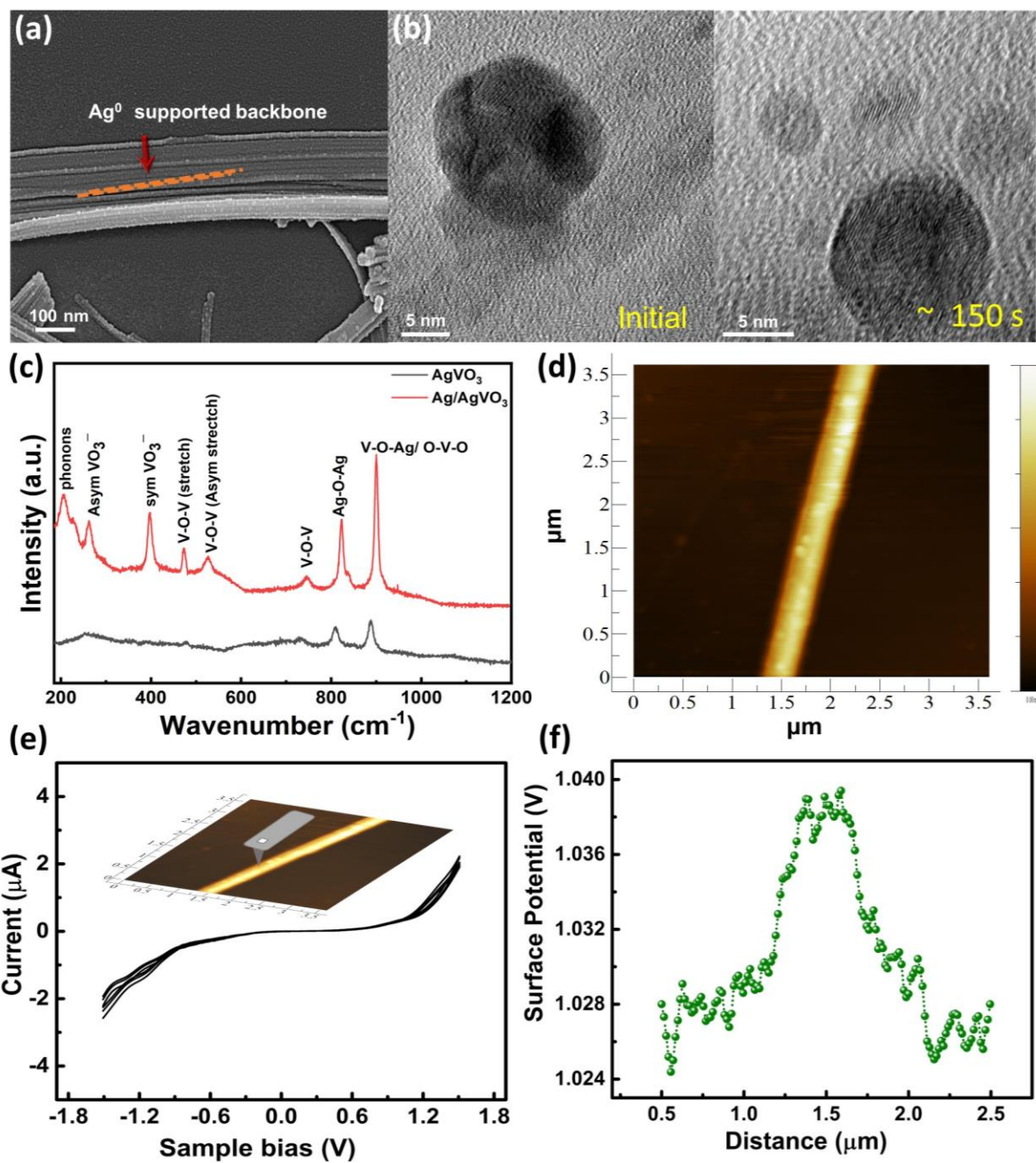


183 The nanoribbon's surface dynamics helps us to examine the transition state at high spatial  
184 resolution using TEM. The Ag fractal dendrites in Figure 1 shows that the nucleation occurs  
185 at the interface. Therefore, the transition at the interface area can be interjected with the  
186 addition of interfacial states. Hence, a deeper understanding of the interface enables us to  
187 explore the dynamics involved during the transition. The lattice fringes of the Ag/AgVO<sub>3</sub>  
188 heterostructure interface are obtained using high resolution transmission electron microscope  
189 micrograph, as shown in Figure 2(a). The average diameter of Ag nanoparticle (inset) ranges  
190 from 5-10 nm with a lattice spacing 0.23 nm, corresponds to (111) plane. The nucleated edge  
191 and the growing edge can be seen alongside interface, and the crystal orientations are  
192 different at the interfaces. The corresponding inverse fast Fourier transform (IFFT) image  
193 was generated from high resolution interface and shown in Figure 2(b). Three diffraction  
194 points are masked to simulate the IFFT along the interface. The lattice fringes at the edge  
195 sections-1 & 3 and in the middle segment-2 of the interface show different inter-planar  
196 spacing (Figure 2(c)). The phenomenon shows increase in crystal plane spacing in the  
197 segment -2. The interplanar spacing of 0.59 nm is observed in segment -2, about two times as  
198 long as segments 1 & 3 (~0.29 nm, corresponds to (-601) plane). The crystal plane  
199 corresponding to the lattice spacing of 0.59 nm is not observed in the diffraction pattern from  
200 XRD. This may be due to the introduction of new localized defect states resulting from  
201 thermal fluctuations of the e-beam. The increase in the lattice spacing suggests phase

202 transformation during the growth of Ag crystallite on 1D AgVO<sub>3</sub> surface, confirming the  
203 restructuring process in the nanoribbons. The electron beam may also create extended defects  
204 besides point defects that act as trapping sites for the charge carriers and contribute to band  
205 bending near the surface of the nanoribbons. This phenomenon reduces the bandgap and can  
206 be verified using the UV-Vis and tauc-plots (supporting Figure S3). The UV-Vis spectrum of  
207 irradiated AgVO<sub>3</sub> nanoribbons show a broad absorption spectrum ranging from ultraviolet to  
208 visible. An optical absorption band edge of ~1.59 eV is observed in the absorption spectrum  
209 in contrast to ~2.01 eV reported for pristine AgVO<sub>3</sub>(16). During the in-situ process, the  
210 hybridization of Ag 5s orbital with Ag nanoparticles occurs, and the bandgap shifts below the  
211 conduction band. Consequently, the bandgap is narrowed, resulting in Ag nanoparticles  
212 conceivably increasing the rate of charge carriers at the interfaces. The broad visible  
213 absorbance can be attributed to the SPR effect of bonded Ag<sup>0</sup> nanoparticles on the surfaces of  
214 AgVO<sub>3</sub> nanoribbons. A representative high-resolution image showing additional interfacial  
215 states is shown in the supporting Figure S4(b). This induced structural modification of  
216 AgVO<sub>3</sub> nanoribbons with extrinsically bounded metal Ag nanostructures enhances the  
217 interfacial charge transfer mechanism by improving the electron-hole separation (28). To  
218 better understand this, electron energy loss spectroscopy (EELS) is performed. Top panel in  
219 Figure 2(d) shows HAADF image shows the point of interest for obtaining the EELS spectra  
220 (Figure 2(e)), bottom panel shows the HR-TEM image with interplanar spacing on the  
221 nanoribbon surface. The EELS spectra corroborate the behaviour observed by HAADF-  
222 STEM images. The potential influence on the specimen surface was analysed by conducting  
223 corresponding EELS experiments. Changes in local chemistry or chemical bonding are  
224 identified by tracking the fine structure of EELS spectroscopic data associated with the local  
225 electronic structure. The EELS spectra obtained from the site with no Ag<sup>0</sup> nanoparticle  
226 formation is marked as 1. Site-1 show two firm peaks at 516.3 eV and 522.7 eV, which

227 matches with Vanadium L3 and L2 edges, obtained from loss spectra during the excitation of  
228 V 2p core states to unoccupied 3d states (L3, transition from  $2p_{3/2} \rightarrow 3d$ ) and L2, transition  
229 from  $2p_{1/2} \rightarrow 3d$ ), due to spin-orbit splitting. However, at the interface of the Ag fractals,  
230 the V L3 and VL2 edges are shifted to higher energies of 518.2 eV and 524.04 eV,  
231 respectively. This shift at the interface can be accounted to the atomic rearrangement with  
232 silver vacancy diffusion and oxide formation in the Ag fractals with the migrated oxygen  
233 species bonded to the silver nanoparticles. Further, the surface of the  $\beta$ -AgVO<sub>3</sub> with Ag  
234 nanoparticles (region 3) has peak shifts at 518.5 eV and 525.1 eV. This suggests the presence  
235 of vanadium in multiple oxidation states. An additional intense peak showing oxygen (O K)  
236 appears from the base region with scarcely contained Ag<sup>0</sup> which shows numerous oxygen  
237 defect sites in comparison to region at the interfacial surface of silver nanoparticles.

238 Scanning electron micrographs in Figure 3(a) & (b)) were used to study the topographical  
239 surface features on the e-beam irradiated nanoribbons. The SEM micrograph shows small  
240 silver nanoparticle clusters resembling nano shell formulations over the core surface serving  
241 as "bridges". These provides path for the matter to move from one site to another during the  
242 e-beam irradiation. Using FEG-SEM, the morphologies of AgVO<sub>3</sub> crystals were examined  
243 with an operating range of 5–15 kV. The electron dose rate was varied at 100-250 e/A<sup>2</sup>s for  
244 the formation and nucleation of Ag NPs on the nanoribbons by adjusting the probe current  
245 and the size of imaging area. Detailed visualization of the diffusion process under cumulative  
246 electron dose in TEM was carried out at various time intervals and recorded (Supporting  
247 Figure S6). The diffusion process further assisted the formation of the Ag lattices from the  
248 initially merged Ag particle surfaces due to the thermal spikes induced on the metal surface  
249 by bombarding high energy electrons (Figure 3(b) left panel t=0, right panel t= $\sim$ 150 s). Thus,  
250 electron beam-assisted segregation of tiny Ag nanoparticles and growth of nanocrystals to



251

252 **Figure 3.** (a) & (b) FE-SEM and TEM micrographs showing the ionization effect on in-situ  
 253 irradiated  $\text{AgVO}_3$  nanoribbon respectively. (c) Raman spectra of the as prepared  $\beta$ -  
 254  $\text{AgVO}_3$  and e-beam irradiated sample ( $\text{Ag}/\beta\text{-AgVO}_3$ ), (d) AFM image of the nanoribbon on  
 255 which the conductive measurements are carried out, (e) I-V characteristics of the nanoribbon  
 256 and (f) surface potential distribution of the ribbon.

257

258 fractal dendrites is thus closely analogous to conventional chemical reduction of nanocrystals,

259 except for the presence of manifold reducing agents or oxidative species. The local defects on

260 the support specimen act as electron trap sites and intensify the reduction of the  $\text{AgVO}_3$   
261 support. The Raman spectra is obtained to determine the vibrational modes of the sample before  
262 and after the e-beam irradiation on the sample as shown in Figure 3(c). The strong band at 887  
263  $\text{cm}^{-1}$  may originate from either-O-Ag or O-V-O vibrations. The band at 810  $\text{cm}^{-1}$  is assigned  
264 to vibrations of the Ag-O-Ag bridges. The bridging V-O-V bond chains is characterized by  
265 the 732, 523 and 480  $\text{cm}^{-1}$  stretching vibrations. The symmetric and asymmetric molecular  
266 signatures of  $\text{VO}_3^-$  are observed at 396  $\text{cm}^{-1}$  and 344  $\text{cm}^{-1}$  respectively, while the symmetric  
267 folding of  $\text{VO}_4^{3-}$  appears at 250  $\text{cm}^{-1}$  representing channelled structure of  $\text{AgVO}_3$ . The  
268 generated Ag nanoparticles result in surface plasmon resonance effect, which is observed  
269 from Raman spectroscopy (Figure 3(c)). The e-beam irradiated sample displayed higher peak  
270 intensities than pristine  $\text{AgVO}_3$  nanoribbon due as a consequence of surface-enhanced Raman  
271 scattering induced by Ag nanoparticles. Figure 3(d) shows the AFM micrograph on which the  
272 conductive measurements were performed. Current-voltage (I-V) curves for a Ti/Ir coated tip  
273 in contact with the nanoribbon is shown in Figure 3(e). All the obtained curves are nonlinear  
274 and symmetric about the axis. The slope of the curve appears linear at low bias voltage of  
275 0.8V. This region is used to evaluate the resistance of the nanoribbon and was found in the  
276 range of  $1.03 \times 10^6 \Omega$  -  $1.42 \times 10^6 \Omega$ . At higher bias, above 1.5V the nonlinearity of curve  
277 increases with sudden ramp in tip current resulting in degradation of the nanoribbon at the  
278 point of contact with AFM tip. Kelvin probe force microscopy was used (29,30) to probe the  
279 surface potential distribution and determine the work function. The surface potential  
280 distribution over the width of the  $\beta\text{-AgVO}_3$  nanoribbons in Figure 3(f) shows uniform surface  
281 potential and charge distribution over the base while the potential distribution decreases  
282 towards the edges of the nanoribbons with a work function of 3.88 eV. An increased  
283 proportion of active electrochemical sites on the surface also effectively decrease the  
284 polarization resistance and shorten the diffusion length.

## 285 **Conclusion**

286 In summary, multifunctional heterostructures were fabricated using an in-situ surface  
287 modification process of 1D  $\beta$ -AgVO<sub>3</sub> by the dynamic growth of Ag nanoclusters using an  
288 imaging e-beam. The nanoribbons with well-organized electron transport chain and many  
289 electroactive species were assembled by modulating the structural and chemical  
290 bonding/interactions. These are associated with in-situ electron beam perturbations and  
291 attributed to  $\beta$ -phase silver vanadate crystals. The dynamics and topological modifications  
292 induced on the nanohybrid interfaces mechanistically suggests the possibility of using novel  
293 hybrid interfaces in harnessing and storing photo generated auxiliary charge carriers. The  
294 synthesis methodology used enables in overcoming major bottleneck in nanoengineering of  
295 solid-solid interfacial heterostructures by providing real-time feedback to precisely fabricate  
296 these heterostructures and study the interface's transition.

## 297 **Methods**

### 298 **Synthesis of solid precursor nanoribbons-**

299  $\beta$ -AgVO<sub>3</sub> nanoribbons were prepared using hydrothermal reaction. Silver nitrate (Sigma-  
300 Aldrich  $\geq 99.0\%$ ) 0.6 mmol and commercially available bulk V<sub>2</sub>O<sub>5</sub> (Sigma-Aldrich, 99.9%)  
301 0.8 mmol were dissolved in 30 mL of deionized water containing 0.1 mM of P123 and  
302 continuously stirred for 3 hrs. 0.2mmol of imidazole (Sigma-Aldrich  $\geq 99.0\%$ ) is added with  
303 continuous bubbling of oxygen. This process leads to the formation of silver imidazole  
304 complex. This suspension is then transferred to a Teflon lined stainless autoclave reactor  
305 vessel and the mixture is kept at 180°C for 3 h. The autoclave is then cooled down to obtain  
306 the final product. The resultant product is washed thoroughly to remove any unreacted  
307 products.



308 **In-situ interfacial manipulation process-** The electron beam manipulation studies on the  
309 nanoribbons were performed using TEM in operating voltages of 200-300 kV under  
310 diffraction and phase-contrast modes. The electron irradiation on the individual nanoribbons  
311 was performed, concentrating the electron beam on circular areas at high-resolution modes  
312 and depend on the size of the particle examined. The samples were initially prepared by using  
313 a specific concentration of AgVO<sub>3</sub> nanoribbons dispersed in acetone via ultrasonication. The  
314 carbon-coated Cu TEM grids were prepared by drop casting the prepared dispersion and  
315 dried in a vacuum. The e-beam intensity was kept constant, varying the irradiation time and  
316 the electron doses with the areas illuminated. The TEM operating conditions in a typical  
317 irradiation experiment were the following: emission current of 184  $\mu$ A: extraction voltage =  
318 4500 V; gun lens = 3; aperture C2 = 70  $\mu$ m with gun and column pressure maintained at  
319  $1.33 \times 10^{-6}$  Pascal and  $1.45 \times 10^{-5}$  Pascal respectively. The restructured nanoribbons under  
320 electron beam exposition were monitored by recording the TEM micrographs using  
321 bright/dark field images at different irradiation times. High-resolution micrographs patterns  
322 were used to study the structural changes. The interfacial manipulation during the reduction  
323 process was monitored using EELS spectra. Using FEG-SEM, the morphologies of AgVO<sub>3</sub>  
324 crystals were examined and low electron dose experiments were performed in operating  
325 voltage range of 10–15 kV.

326 **STEM imaging:** STEM HAADF imaging and the corresponding EELS spectra were  
327 obtained in ambient temperature and cryogenic cooling conditions. In STEM mode for actual  
328 signal measurement, the specimen is focussed and aligned at a neighbouring sacrificial site  
329 and then transferred to the actual location of interest where the sample is unspoiled. A spot  
330 size in the 7-8 has been utilized, and the electron beam's current density and convergence  
331 angle are controlled with the condenser lenses and apertures. In STEM mode, HAADF  
332 images were acquired with a tiny camera length to ensure that only electrons deflected by

333 angles more significant than 50 mrad were acquired by the annular dark field detector. The  
334 HAADF-STEM images were acquired with a convergence of 30 mrad and a collection semi-  
335 angle of 50-200 mrad. The EELS microanalysis was performed by acquiring the signal in  
336 image mode with 15 mrad collection angle.

337 Further, for cryo-mode TEM experiments, plunge freezing methodology is adopted for  
338 sample preparation. A few drops of nanoribbon specimen dispersed in deionized water were  
339 pipetted out onto a bare copper grid. The copper grid was then blotted with filter paper  
340 immediately before plunging it directly into a liquid nitrogen bath. The TEM grid was then  
341 carefully mounted onto a cryo-holder of TEM. A crucial element for low-temperature  
342 observation is achieved through installing a specific cold trap, which effectively prevents  
343 vapour deposition on Cryo-holders and the specimens while in the column.

#### 344 **Material Characterizations**

345 The nanostructure, surface morphologies and e-beam experiments on sample were  
346 characterized using a field-emission scanning electron microscope (JEOL JSM-7600F FEG-  
347 SEM) equipped with EDS for elemental mapping and a high-resolution transmission electron  
348 microscope (FEI, Technai G2) equipped with EELS (Model 965, GIF Quantum) and  
349 multipurpose JEOL, JEM-2100 F. Powdered X-ray diffraction (XRD) was performed in the  
350  $2\theta$  range of 5-80° at a scan speed of 4 min<sup>-1</sup> (Panalytical X'Pert Pro with Cu K $\alpha$  irradiation  
351 with a wavelength of 0.1542 nm). The height and conductivity of nanoribbon is measured  
352 using atomic force microscope (Asylum instruments, MFP3D). The vibrational modes of the  
353 sample were found using Raman spectroscopy (HR-800-UV confocal micro-Raman  
354 spectrometer). To find the functional groups FTIR spectroscopy is carried out using a  
355 spectrometer (3000 Hyperion Microscope with Vertex 80 FTIR System, Bruker). The surface  
356 chemical composition and valance states were examined by X-ray photoelectron

357 spectroscopy (XPS) (AXIS SUPRA) with an Al K $\alpha$  radiation. The electrochemical evaluation  
358 was carried out on Gamry, Interface 5000E.

359 **KPFM mode:** The surface potential of the specimen was evaluated on the surface of single  
360 nanoribbon in amplitude mode which shows a positive potential. The contact potential  
361 difference measured between the conducting AFM tip and the nanoribbon surface. During the  
362 investigation the probe is mechanically driven at a resonant frequency above the nanoribbon  
363 at a definite distance. A static compensation bias is applied which nullifies the electrostatic  
364 forces and therefore the potential becomes equal in magnitude to the contact potential  
365 difference ( $V_{cd}$ ) between tip and sample. For I-V measurements the tip is initially calibrated  
366 with HOPG. The I-V measurement is repeated over a single crystal nanoribbon over 6 times  
367 by scanning the bias voltage at ambient temperature in air. The work function of the sample is  
368 given by  $(\Phi_s) = \Phi_t - eV_{cd}$ , where  $\Phi_t$  is work function of tip and  $e$  is the electronic charge.

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372

### 373 **Declaration of interests**

374 The authors declare no competing interests

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