Electronic Supplementary Material (ESI) for CrystEngComm.
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Supplementary information

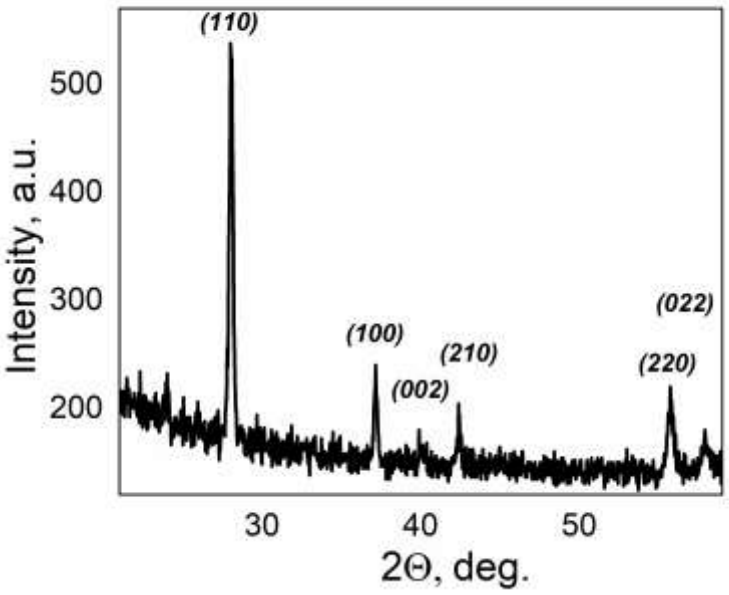

Fig. S1. Typical XRD pattern of the VO_2 film synthesized under optimal growth conditions on the flat surface of the Si structure. This spectrum was taken from the structure with a sharp tip shown in Fig. 2b. The graph shows the directions of the diffraction planes due to the M-phase of VO_2.

A1. Qualitative discussion of the nucleation process of VO_2 NCs on flat and curved surfaces

The growth of the largest VO_2 crystal on the tip apex can be phenomenologically explained considering the nucleation and growth kinetics of VO_2 on a sharp tip. In the case of nucleation on a flat substrate, the surface concentration of crystals (N_C) is proportional to the precursor concentration near the surface and to the nucleation probability

$$P_N = B \cdot \exp\left(-\frac{\sigma^2 \cdot \pi}{k_B^2 \cdot T^2 \cdot \ln \alpha}\right), \quad (1)$$

where B is a constant, k_B is the Boltzmann constant, α is the vapor supersaturation, T is the synthesis temperature, and σ is the free energy of the surface [1,2]. After the formation of a nucleus whose radius exceeds the critical nucleation radius, a VO_2 crystal forms. Then, the VO_2 crystal starts growing; it increases in size and acquires a characteristic crystal faceting. Both the growth rate and the faceting of the crystals depend on the concentration of adparticles and their surface diffusion length λ_a. The diffusion length of adparticles is given by the expression

$$\lambda_a = \sqrt{D_0 \cdot \exp\left(-\frac{E_{diff}}{k_B \cdot T}\right) \cdot \tau}, \quad (2)$$

where D_0 is a constant, E_{diff} is the activation energy of surface diffusion, and τ is an effective lifetime of adparticles on the surface. Relatively low concentrations of adparticles and their large diffusion lengths lead to a slow crystal growth. Adparticles migrate to the crystal faces with a high free surface energy and get incorporated into them. As a result, the VO_2 crystals predominantly grow along the direction [100] of their most rapid growth to form VO_2 nanowires [3,4]. On the contrary, a high concentration of adparticles and their short diffusion length lead to a rapid crystal growth. Adparticles have a short lifetime and they get incorporated into the VO_2 crystals on the surfaces they have first appeared. As a result, there grow dendrite-like VO_2 crystals [5,6].

In our study, the synthesis conditions were chosen such that to obtain an intermediate rate of crystal growth with equilibrium morphology of the crystal (such morphology can be obtained using the standard Wulff construction). The latter is supported by the SEM data concerning the surface morphology of the VO_2 polycrystalline films grown on the planar side surfaces of the tips.

In the formation of nucleation centers on the tip apex, in addition to the small area on which the nucleation proceeds, there exists another important factor, namely, the local temperature of the tip apex, this temperature normally being slightly lower than the temperature of the flat substrate. According to formula (1), a lower tip-apex temperature leads to a lower nucleation probability of VO_2 NCs. This means that, at all other conditions being identical, the number of nuclei per unit area should be lower on the tip apex compared with the flat surface. This, ceteris paribus, can lead to a selective synthesis of single VO_2 NC on the tip apex of nanosharp tip, in contrast to the formation of polycrystalline VO_2 film on the flat surface of the same structure.

A2. Growth of several VO_2 NCs on non-sharp tip apices

Among other things, the number of nucleation centers for VO_2(M) NCs depends on the synthesis conditions. Based on formula (1), it can be speculated that, by varying the growth temperature, one can control the number of nuclei per unit area. However, when attempting realization of conditions for the formation of exactly one nucleation center on a tip apex, one can find the quality of the top VO_2 crystal obtained seriously degraded. Therefore, a more important parameter here is the ratio between the tip-apex curvature radius and the diffusion length λ_S of adparticles on the tip surface. In order to estimate the necessary sharpness of the tip apex on which only one VO_2 NC will grow, we took in consideration the mean distance between the neighboring nucleation centers in a typical polycrystalline VO_2 film. Indeed, if the diffusion length λ_S of VO_2 adparticles on the tip surface is greater than the linear size of the tip apex, then only one VO_2 crystal will appear on it. The diffusion length is approximately given by one-half of the average distance between the growing nuclei [7,8]:

$$\lambda_S = \frac{1}{2 \cdot \sqrt{N_C}}, \qquad (3)$$

where N_C is the surface concentration of the crystals. It can be seen from the SEM images that the mean distance between the neighboring VO_2 crystals on the side surfaces of the tips is approximately 200 nm. It follows from here that the characteristic tip-apex size should be less than 100 nm. To confirm the importance of tip geometry (namely, the effect due to the presence of a sharp tip apex on the growth of the VO_2 single crystal), the synthesis of VO_2 on the tips with broken apices was attempted.

Figure S2a shows a specially broken Si tip. After the breaking of the tip, an area with a typical linear size of 100 nm was formed on the tip apex. Our attempts to synthesize single VO_2 NCs on such tips were always a failure. From Fig. S2b, it is clearly seen that, on the broken tip, at least three VO_2 NCs started growing. The characteristic sizes of these NCs were roughly identical to the crystal sizes of VO_2 crystals on the side surface of the tip. Hence, our estimate of tip sharpness proved to be consistent with the experiment on the synthesis of VO_2 NCs on the broken tips.

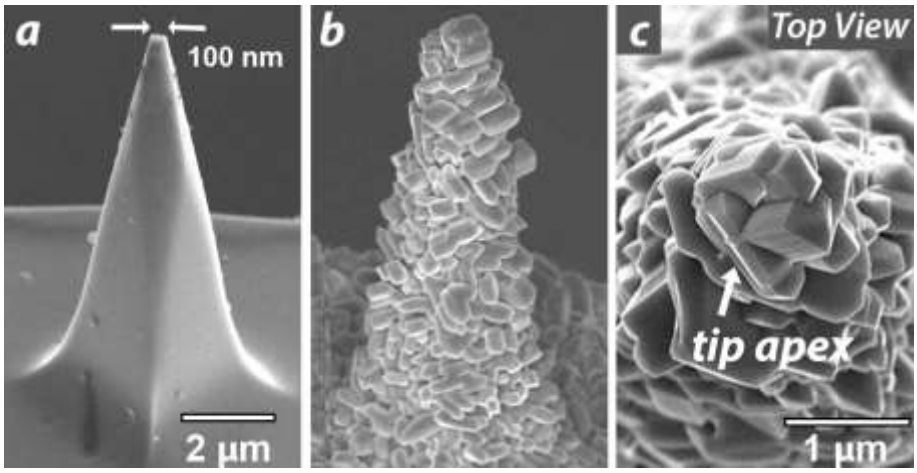

Fig. S2. SEM images of a Si tip with a broken tip (area with a typical linear size of 100 nm). a) initial Si tip. b) the same tip after a 4-hour synthesis of VO_2 at a temperature of 453 ^oC. c) top view of the tip. It is seen that several competing crystals grew simultaneously on the broken tip.

Thus, the involvement of sharp structural features with a small curvature radius on which the nucleation of a single VO_2 NC occurs is an important factor defining the outcome of the experiments on the MOCVD growth of VO_2 NCs. Moreover, this conclusion applies not only to the sharp tips but, also, to the case of small flat surface areas. Indeed, it was shown that only one nucleus of VO_2 could be formed on a 80-nm wide square Si nanopedestal during the synthesis of vertically aligned VO_2 nanowires [9].

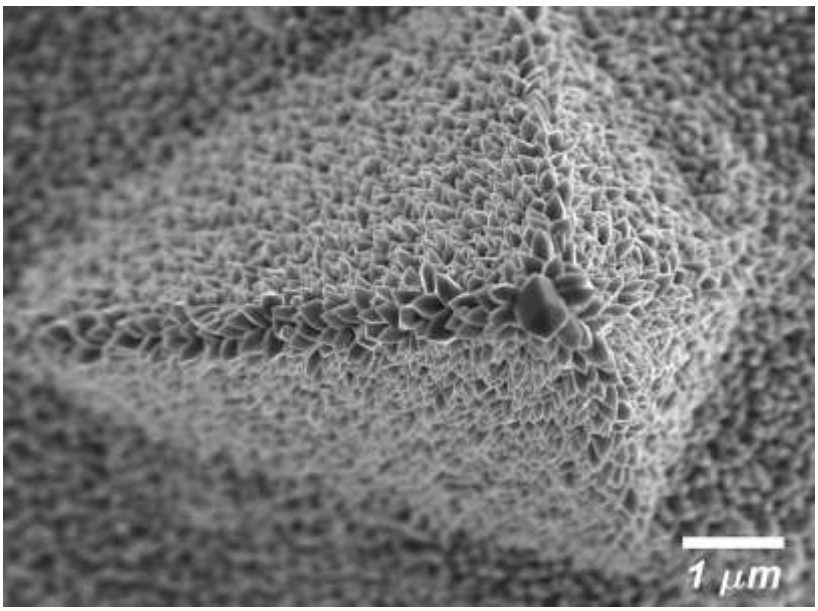

Fig. S3. Top view of a pyramidal-shaped nano-sharp Si tip with VO_2(M) nanocrystals grown on this tip at 453 ^oC during 240 minutes. An enlarged image of the tip apex is shown in Fig. 3c of the article. It is clearly seen that almost all VO_2 crystals had a pen-like shape typical of the VO_2(M) phase, and they grew in the direction normal to the tip surface. The largest crystal grew on the tip apex. Similarly, the crystals synthesized on the sharp tip edges were larger than the crystals grown on the lateral faces of the tip. The large crystal sizes can be attributed to the absence of competition between neighboring crystals for the growth material. Note that the size, the shape, and the density of the crystals show no variation over the tip surface, from its base to tip apex, both on the lateral faces of

the tip and on its edges. This indicates that the growth conditions were identical throughout the tip (the height of the tip was 14 μm). This was due to the high thermal conductivity of Si (1.3 W $cm^{-1} \cdot C^{-1}$).

A3. Long-term selective synthesis of a VO_2 NC on the tip apex

Consider qualitatively the main factors that determine the shape and faceting of crystals. First, according to (2), the diffusion length of adparticles depends on the local temperature. A lower temperature leads to a shorter diffusion length. Second, there is a relationship between the size of the crystal and the diffusion length of the adparticles in the formation of crystal faceting. If the crystal is small in comparison with the diffusion length of adparticles, then almost all adparticles will have enough time to find a most favorable place for themselves in the growing crystal. In the latter case, the crystal faces will have a smooth surface and a distinct faceting. On increasing the linear crystal size, the diffusion length remains unchanged. If the crystal grows large compared to the diffusion length, then most adparticles do not have enough time to find the favorable places for themselves in the growing NC. In this case, the crystal faces with high surface energy (forming the prismatic portion of the crystal) may be rougher than the faces with low surface energy (forming the flat side walls of the crystal).

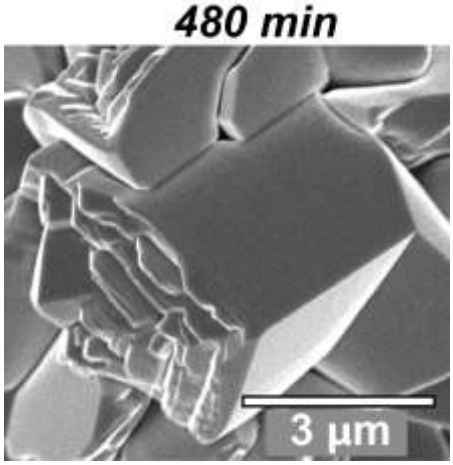

Fig. S4. VO_2 crystal synthesized on the tip apex under the optimum synthesis conditions for 480 min (top view). The synthesis was performed on a tip of the same type like that shown in Fig. 5 of the article.

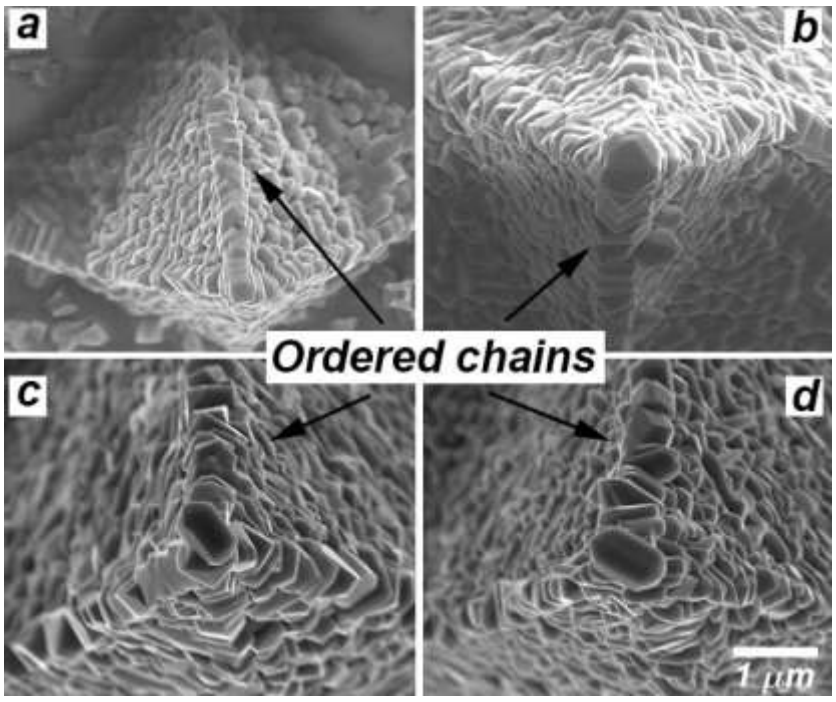

Fig. S5. SEM images of the tips with VO_2 NCs, top view. Examples of the ordered growth of VO_2 NCs along the sharp edges of pyramidal silicon tips. It is seen that, in each of the images, the VO_2 NCs form crystal chains stretching along each sharp edge of the tip. The crystal size in the chain is larger than the mean crystal size on the flat surface of the tip. The largest crystal is located at the tip apex (approximately at the center of each image).

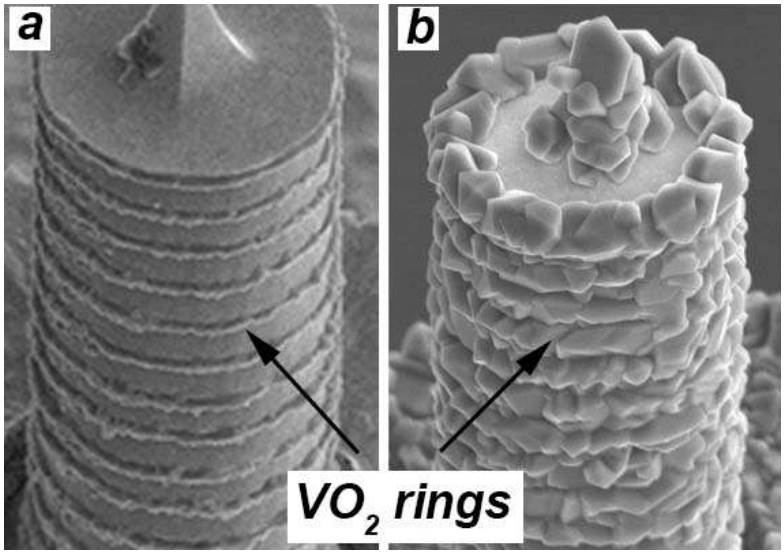

Fig. S6. SEM images of a Si tip shaped as a cylinder with sidewall scallops having sharp edges. Side view. An additional example to Figs. 6 (c,d,e) of the article illustrating the selective synthesis of VO_2 on structures obtained using a Bosch process and exhibiting a good reproducibility of the synthesis of VO_2 nanorings. a) Synthesis of VO_2 rings during 60 minutes, b) synthesis of VO_2 rings during 180 minutes.

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