Supporting Information

Synthesis and Phase Stability of Metastable Bixbyite V_2O_3 Colloidal Nanocrystals

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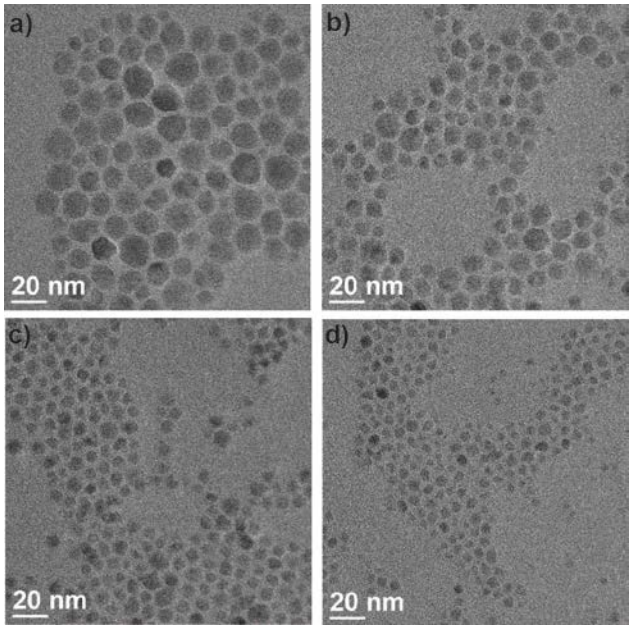

Figure S1. Small nanocrystals separated from nanoflowers by size selective precipitation with average diameter a) 12.0 ± 3 nm, b) 8.0 ± 2 nm, c) 6.1 ± 1.2 nm, and d) 4.5 ± 1.0 nm.

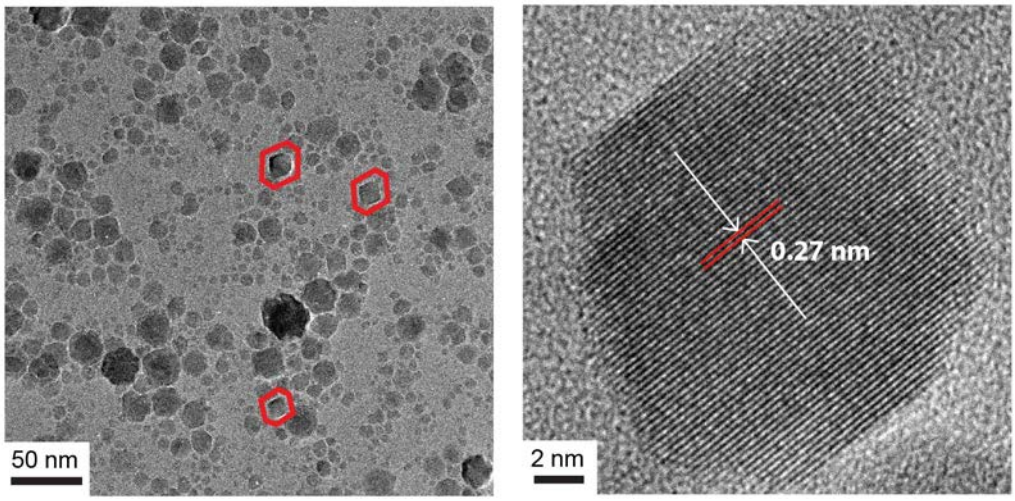

Figure S2. Faceted nanocrystals form at elevated temperatures (370°C and above). Lattice spacing of 0.27 nm matches spacing between (222) planes in the bixbyite structure. XRD scan can be indexed to pure bixbyite phase.

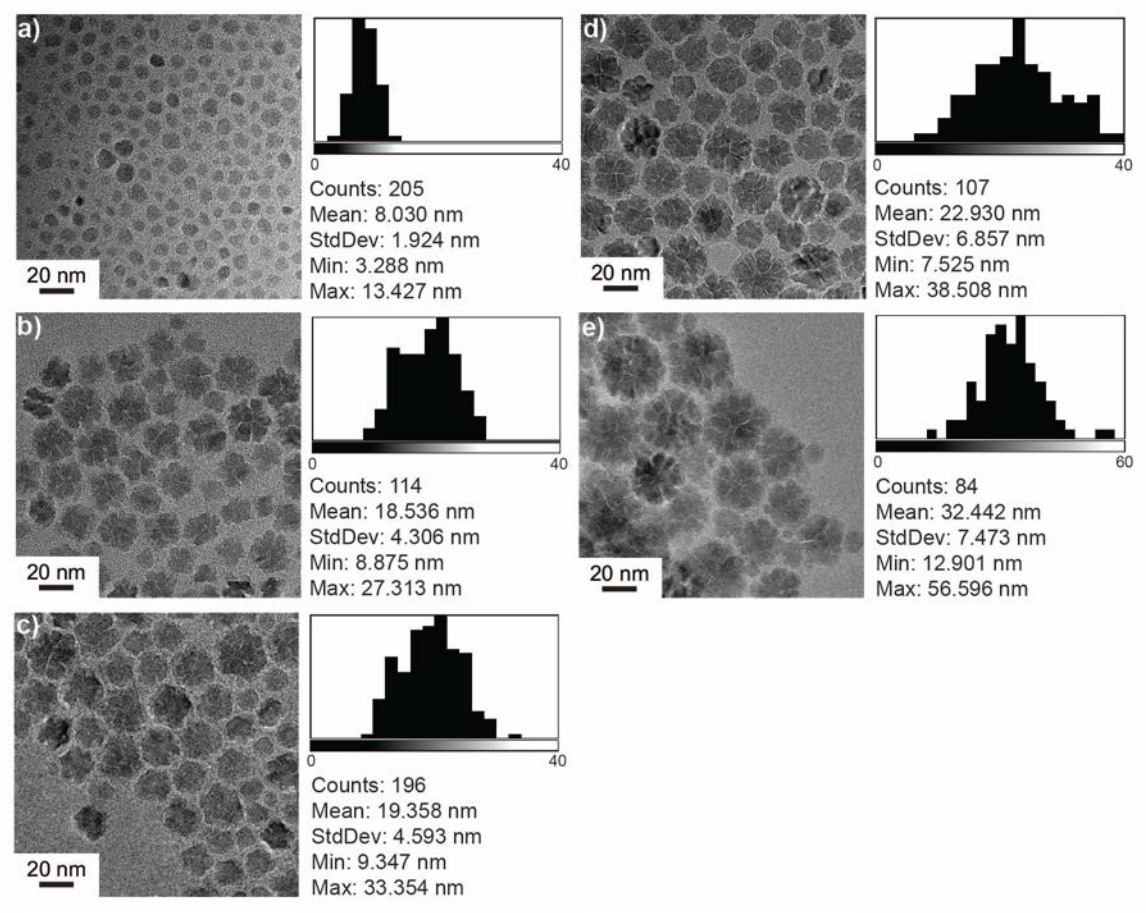

Figure S3. Histograms showing size distribution of nanocrystals synthesized at 340°C for a) 0 minutes with fast quench, b) 0 minutes with slow cooling, c) 1 hour, d) 4 hours, and e) 24 hours

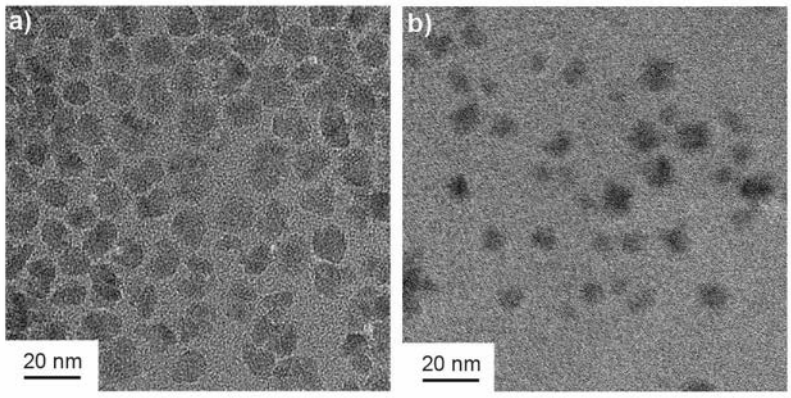

Figure S4. TEM images of nanocrystal made with a) excess oleylamine (6 mmol oleylamine with 4 mmol oleic acid) and b) excess oleic acid (6 mmol oleic acid with 4 mmol oleylamine).

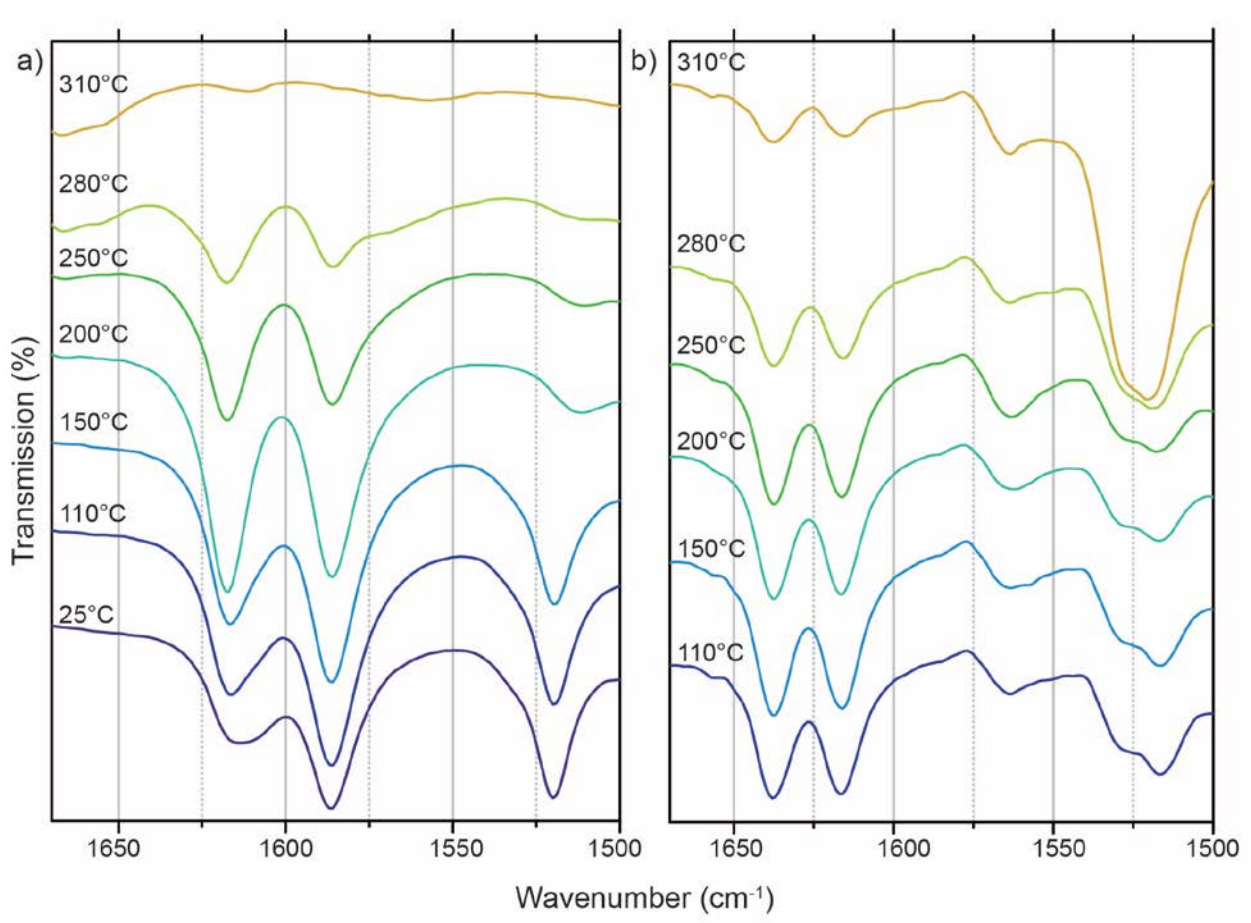

Figure S5. FT-IR spectra of reaction mixture collected at various temperatures during the heating of the reactants without the addition of a) oleic acid and b) oleylamine.

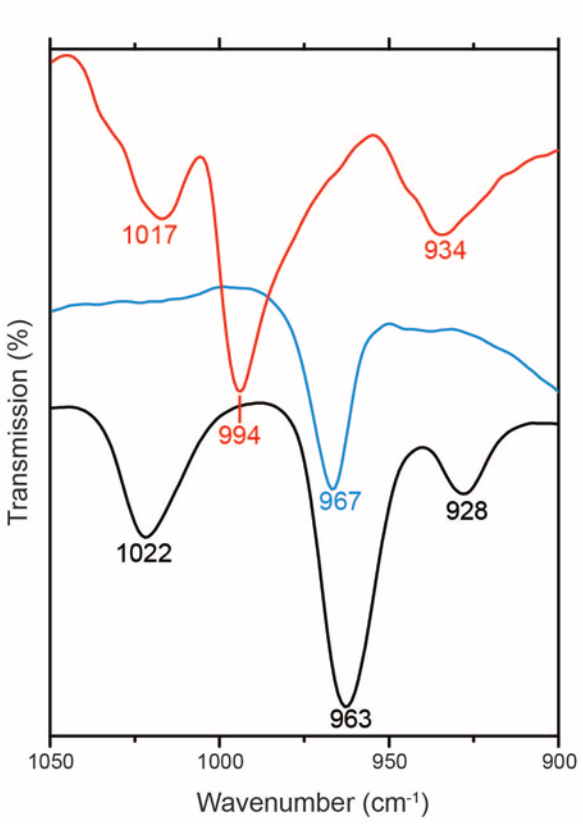

Figure S6. FT-IR spectra of vanadyl acetylacetonate (red), oleylamine (blue), and a mixture of 1 mmol vanadyl acetylacetonate and 4 mmol oleylamine stirred at room temperature until completely dissolved (black). The V=O stretch peak, originally located at 994 cm^{-1} in vanadyl acetylacetonate, shifts to either lower or higher wavenumber in the oleylamine mixture (963 cm^{-1} or 1022 cm^{-1}). This is evidence of a change in ligand binding environment surrounding the vanadyl ion, therefore supporting the hypothesis that oleylamine and vanadyl acetylacetonate form a complex in solution. The peak at 1017 cm^{-1} in the vanadyl acetylacetonate can be indexed to the CH_3 rocking absorption, the peak at 967 cm^{-1} in the oleylamine is the C-H out of plane bend in C=C-H, and the peaks at 934 and 928 cm^{-1} is the C-CH_3 stretch.

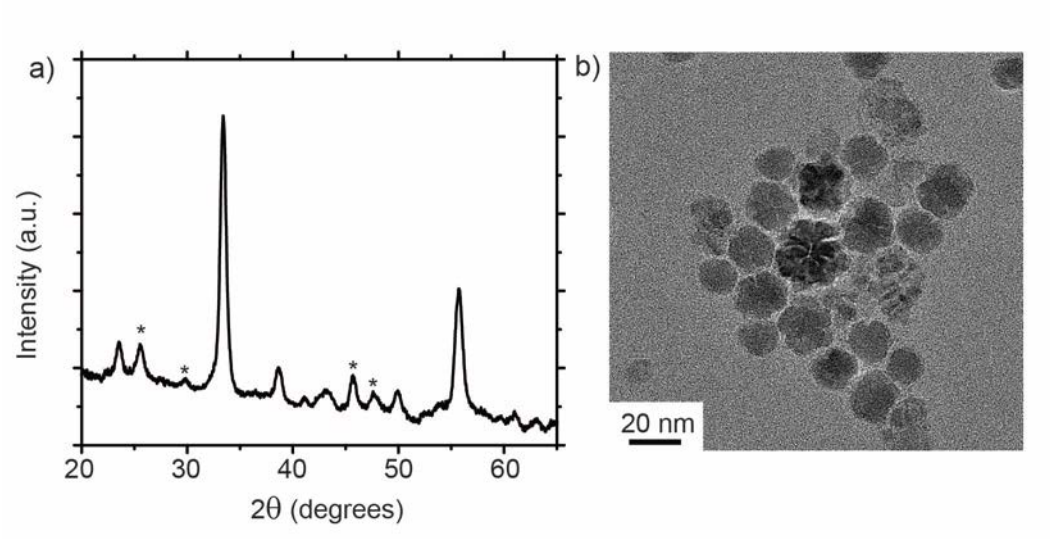

Figure S7. a) XRD pattern and b) TEM image of nanocrystals synthesized with 2 mmol oleic acid and 2 mmol oleylamine. The nanocrystal morphology and size do not appear to be different than those made using 4 mmol oleic acid and 4 mmol oleylamine. An impurity phase (*) evident in the XRD scan can be indexed to the metastable VO_2-A phase. The data was modeled using the program Crystal Diffract and was found to contain approximately 75% bixbyite phase and 25% VO_2-A phase.

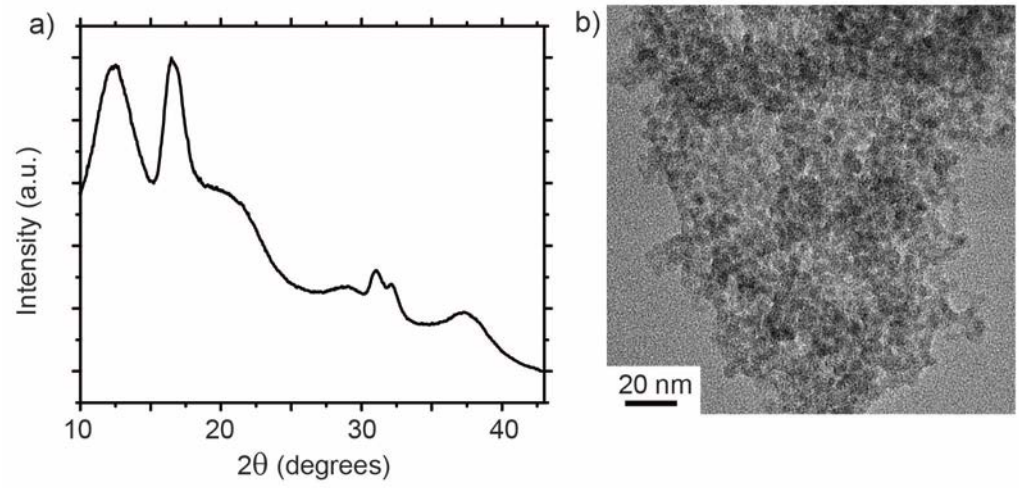

Figure S8. a) XRD scan and b) TEM image of nanocrystals synthesized using 4 mmol oleylamine and no oleic acid. The XRD scan cannot be indexed to any known phase. The TEM shows a network of small (~5 nm) nanocrystals.

Table 1. Results of Rietveld Refinement

Crystal Dimensions	5-30 nm
Crystal System	Cubic
Space Group	I a -3
Unit Cell Dimensions	a= 9.36337(8) Å
Unit Cell Volume	820.911(22)$Å^3$
Calculated Density	4.852 g/cm^3
2θ range	15-80°
Radiation	Cu Kα 1+2
Wavelength	1.541 Å
Temperature of Measurement	25°C
Absorption corrections performed?	yes
Method of Refinement and Program	GSAS + EXPGUI
Number of Refined Parameters	14
Rp	1.75%
Rwp	2.31%
χ^2	2.339

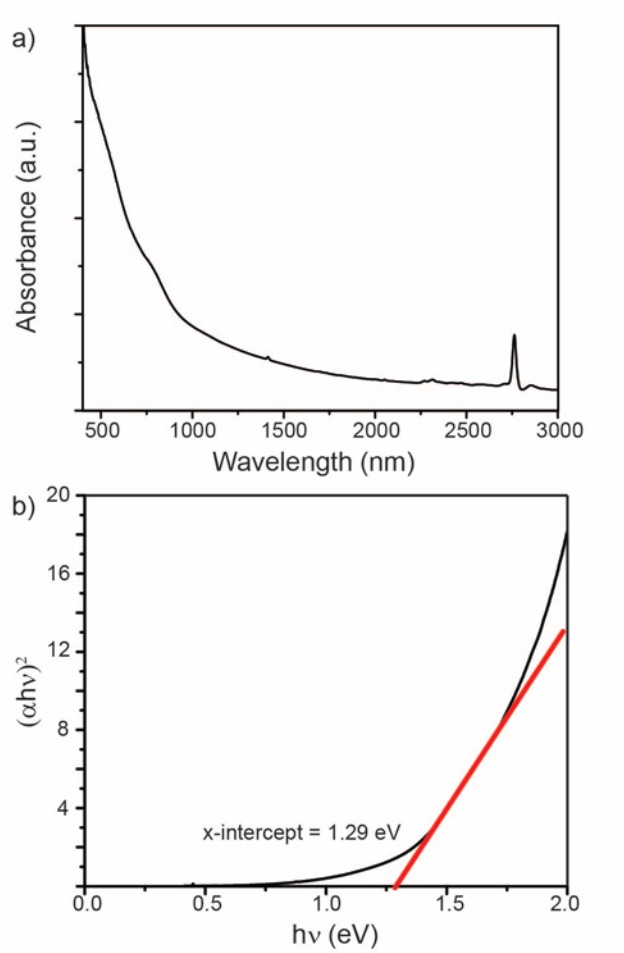

Figure S9. a) UV-Vis spectra of bixbyite nanocrystals suspended in tetrachloroethylene. b) $(\alpha h\nu)^2$ plotted versus energy in order to determine the direct band gap, which was found to be 1.29 eV.

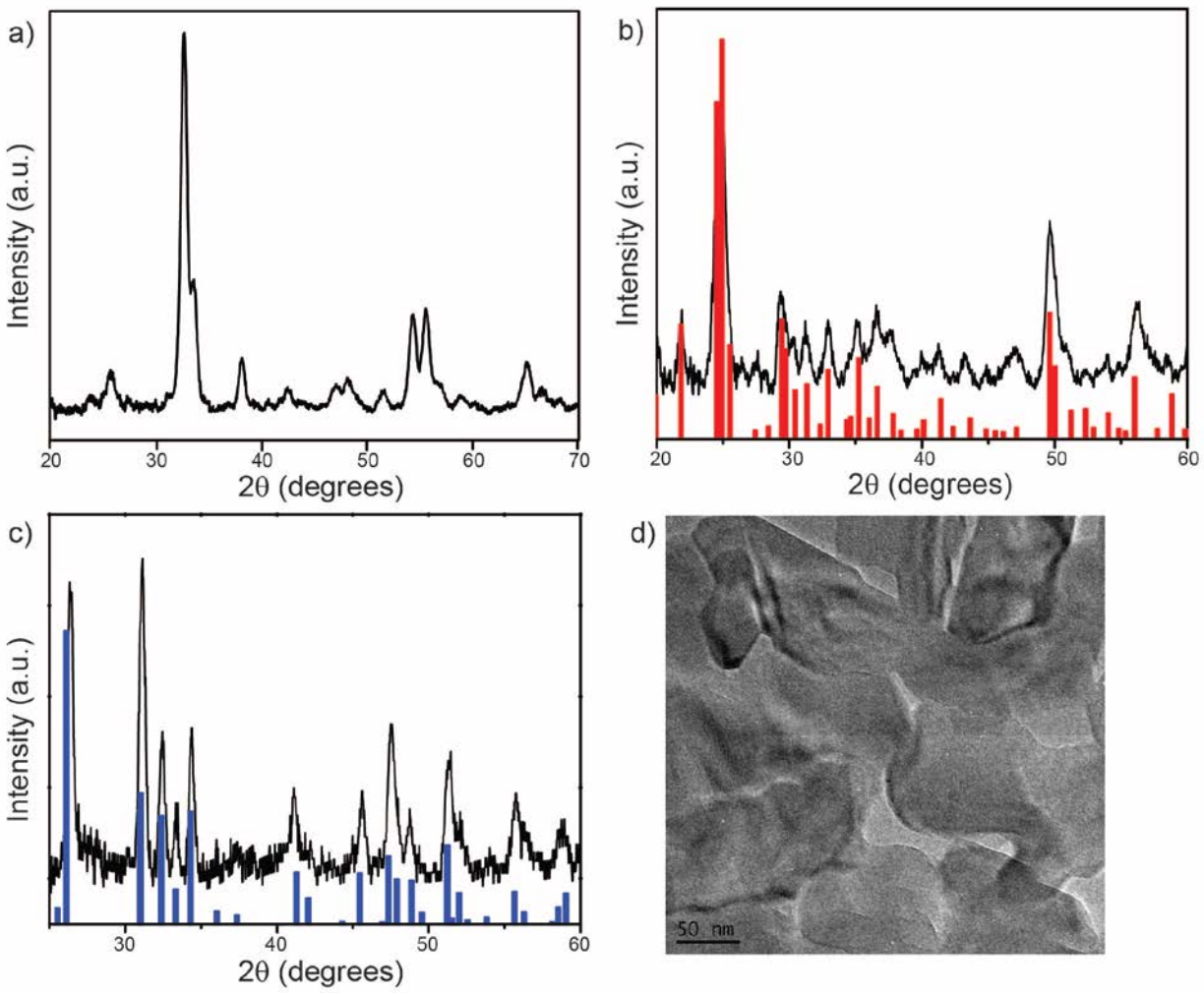

Figure S10. XRD patterns of bixbyite nanocrystals after annealing in air for a) 12 hours 100°C and for 30 minutes at b) 300°C, and c) 400°C. The red and blue lines indicate the position of the XRD peaks for V_3O_7 and V_2O_5, respectively. No further oxidation occurs above 400°C. d) TEM image of bixbyite nanocrystals on SiN grid after annealing at 400°C for 30 minutes (see Figure 2c for TEM of as-deposited nanocrystals)

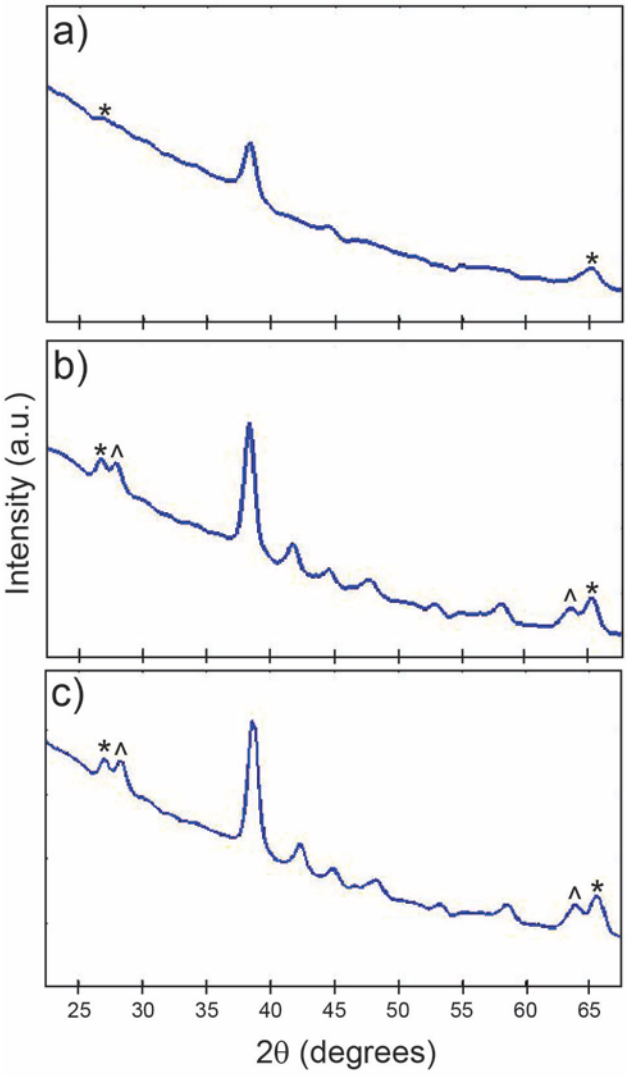

Figure S11. XRD scan before heating ramp, after heating ramp and hold for 30 minutes at 700°C, and after cooling to room temperature. Unique bixbyite peaks marked with * and rhombohedral peaks marked with ^.