Supporting Information

Surfactant Controlled Growth of Niobium Oxide Nanorods

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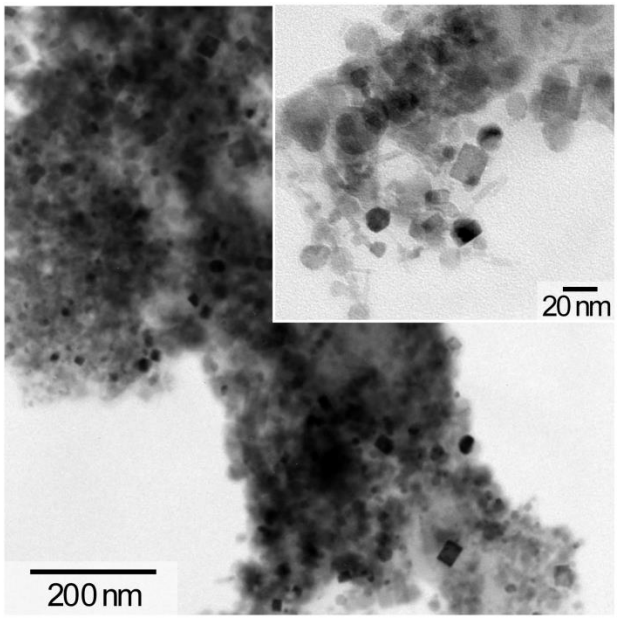

Figure S1. Oleylamine assisted growth of Nb_2O_5 nanostructures prepared at a lower pH (adding 400 µL of 1% HCl), which created an ionic form of oleylamine ($R\text{-}NH_3^+Cl^-$). The drop in pH of the reaction dramatically altered the morphology of the final product as observed by these transmission electron microscopy (TEM) images.

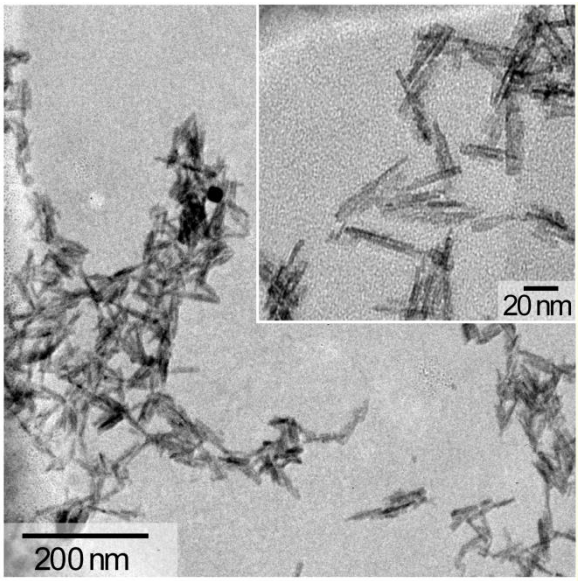

Figure S2. Prior to heat treatment in the autoclave, the synthesis containing cetyltrimethylammonium bromide (CTAB) shows the presence of rod-like features as observed by TEM.

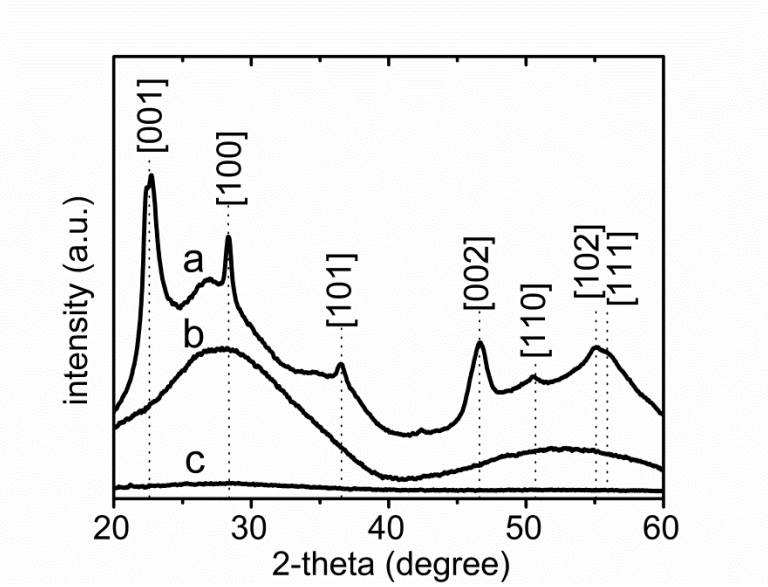

Figure S3. X-ray diffraction (XRD) patterns of: (a) the crystalline Nb_2O_5 nanorods prepared by processing the mixture of niobic acid and CTAB at elevated temperatures in an autoclave; (b) niobic acid in the presence of CTAB before heat treatment in an autoclave; and (c) the sample holder. The XRD pattern is indexed for pseudo-hexagonal Nb_2O_5 (JCPDS No. 028-0317).

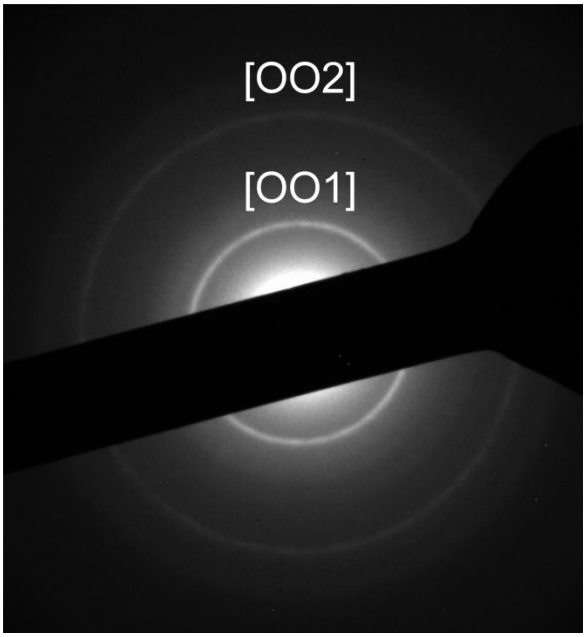

Figure S4. Electron diffraction pattern of niobium pentoxide nanorods. This diffraction pattern corresponds to Nb_2O_5 with d-spacings of 3.9 Å and 1.9 Å for [001] and [002], respectively. This analysis is in agreement with the measurements obtained by HRTEM of lattice fringe patterns and XRD analyses, as well as to the reference material for pseudo-hexagonal Nb_2O_5 (JCPDS No. 028-0317).

Analyses of Purified Nb_2O_5 Nanorods by Raman Spectroscopy

A series of Raman spectra were acquired for purified samples of nanorods using a Renishaw inVia Raman microscope with a 50x LWD lens (0.5 NA) and a 514 nm laser excitation at 100% laser power. The samples were mounted as powders on a glass microscope slide (Leica 1 mm Surgipath Snowcoat X-tra Micro Slides). Raman spectra were separately acquired for the region from 1000 cm^{-1} to 100 cm^{-1} and from 1800 cm^{-1} to 1000 cm^{-1} with exposure times of 60 s and 300 s, respectively. The presence of characteristic Raman scattering bands in the region between 1800 cm^{-1} to 1000 cm^{-1} associated with different functional groups indicated the presence of various surfactant molecules.

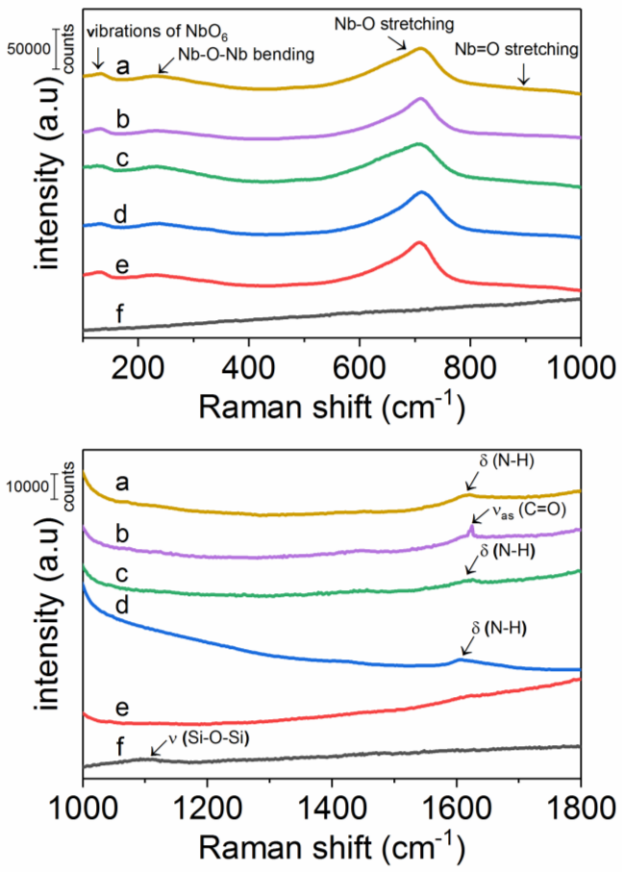

Figure S5. Raman spectroscopy result obtained over two spectral regions (top plots are from 100 to 1000 cm^{-1}, and bottom plots are from 1000 to 1800 cm^{-1}) of Nb_2O_5 nanorods prepared in the presence of (a) poly(allylamine hydrochloride) or PAH, (b) polyvinylpyrrolidone or PVP, (c) cetyltrimethylammonium bromide or CTAB, and (d) cis-1-amino-9-octadecene or oleylamine. Control samples included (e) Nb_2O_5 nanorods prepared without the addition of surfactants to the reactants, and (f) a typical Raman spectrum of the glass slides used as a substrate for the samples during these analyses.

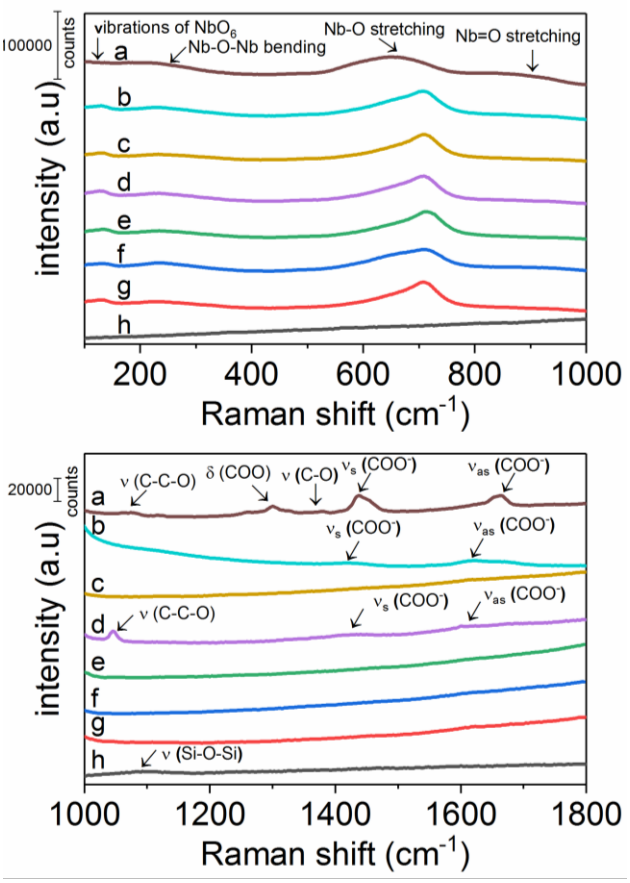

Figure S6. Raman spectroscopy result obtained over two spectral regions (top plots are from 100 to 1000 cm^{-1}, and bottom plots are from 1000 to 1800 cm^{-1}) of Nb_2O_5 nanorods prepared in the presence of (a) trisodium citrate, (b) citric acid, (c) cis-9-octadecanoic acid or oleic acid, (d) poly(acrylic acid) or PAA, (e) sodium dodecyl sulfate (SDS), and (f) poly(sodium 4-styrenesulfonate) (PSS). Control samples included (g) Nb_2O_5 nanorods prepared without the addition of surfactants to the reactants, and (h) a typical Raman spectrum of the glass slides used as a substrate for the samples during these analyses.

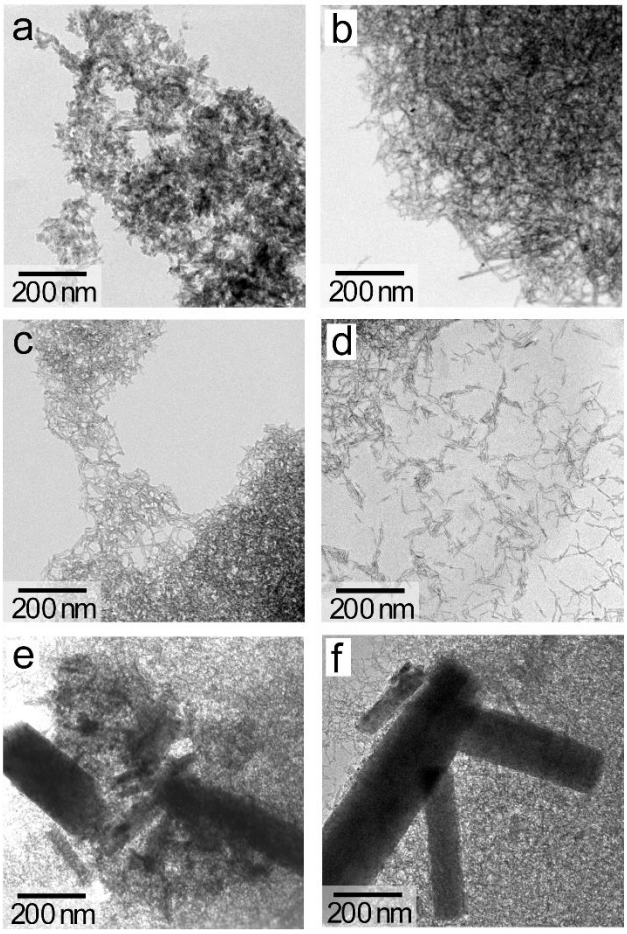

Figure S7. Transmission electron microscopy images of niobium oxide nanorods after a 24 h synthesis at 200 °C. Nanostructures in (a), (b), (c), (d), and (e) were synthesized from solutions containing 100, 10, 1, 0.1, or 0.01 mM sodium dodecyl sulfonate (SDS), respectively. The product in (f) was synthesized without the addition of any surfactants.

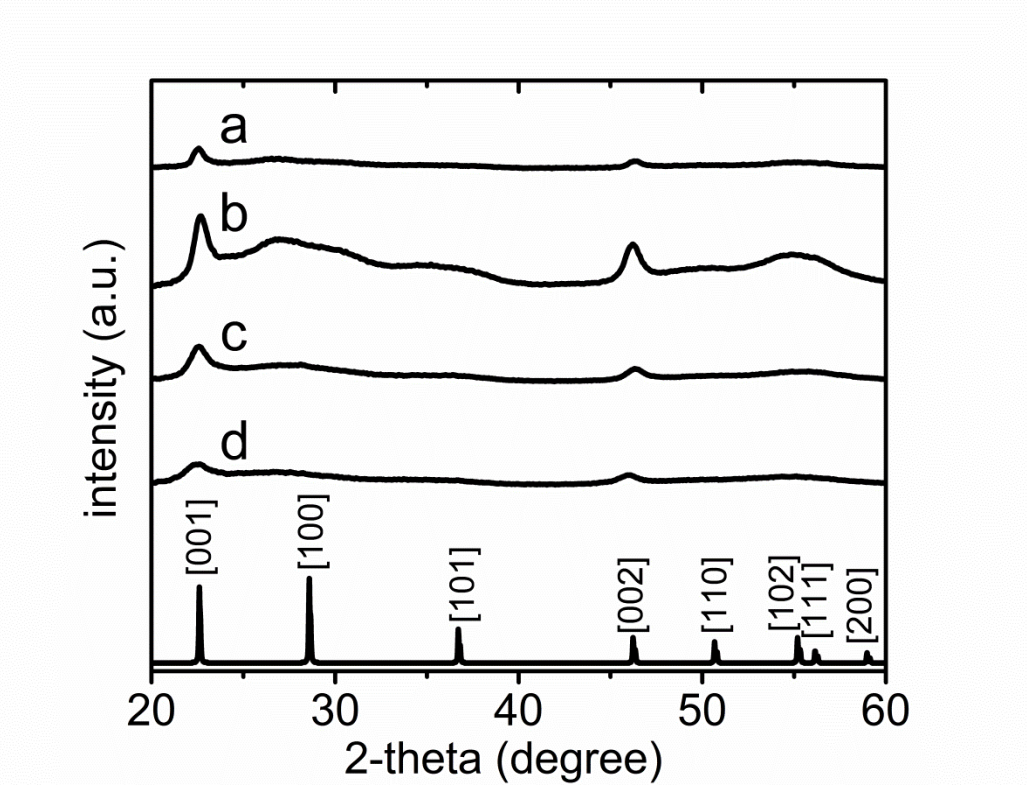

Figure S8. X-ray diffraction analyses of niobium oxide nanorods synthesized in the presence of SDS at concentrations of: (a) 0.1 mM; (b) 1 mM; (c) 10 mM; or (d) 100 mM. A fully indexed reference XRD pattern is also included for pseudo-hexagonal Nb_2O_5 (JCPDS No. 028-0317).

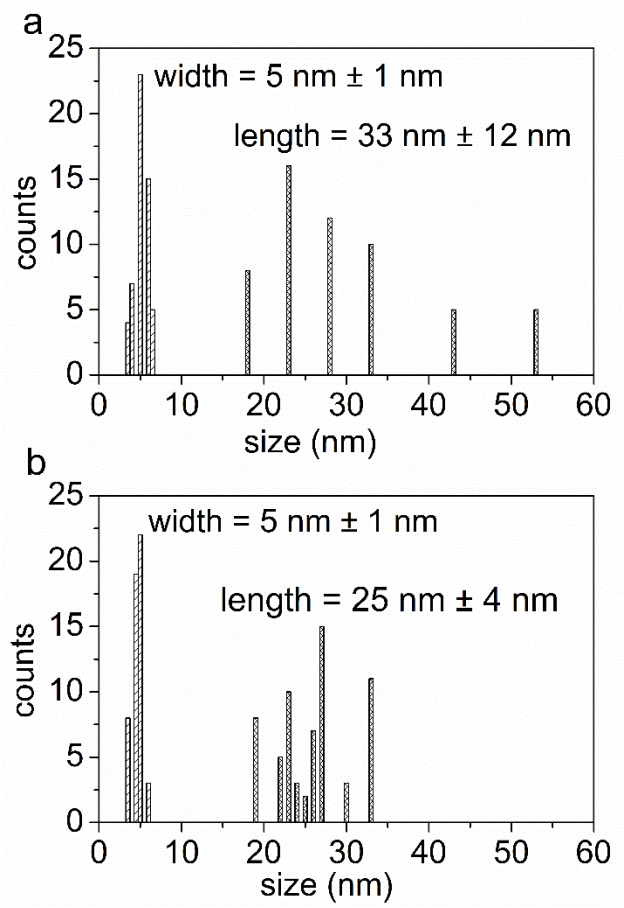

Figure S9. Histograms showing the width and length of niobium oxide nanorods synthesized (a) without any surfactant (excluding the dimensions of the much larger rod-like structures), and (b) in the presence of 1 mM SDS. The nanorods prepared without surfactant had an average aspect ratio of 6.6, while those prepared with 1 mM SDS had an aspect ratio of 5.

Table S1. Published results for the critical micelle concentrations (CMCs) for some of the surfactants used in this study.

surfactant	CMC (mM)	references
CTAB	1	1,2
OA	0.72 to 3.5	3
PSS	0.06	4
SDS	8.2	1,2

Analysis of Micellar Assemblies of SDS by Dynamic Light Scattering Techniques

Three different aqueous solutions were prepared with either 1.0, 8.2 or 16.0 mM SDS. The CMC of SDS is 8.2 mM (Table S1).[1,2] Micellar assemblies of SDS may serve as soft templates for the formation of the nanocrystalline particles of Nb_2O_5, which subsequently assemble into nanorods through a process of oriented attachment. Changes to the concentration of the SDS above or below the CMC could result in a change in the dimensions of these soft templates. These presence and size of these templates were analyzed by dynamic light scattering (DLS) techniques using a Zetasizer Nano ZS from Malvern Instruments. The samples were held in 2 mL volume plastic cuvettes, and all DLS measurements were conducted at 25 °C. A relatively high yield of nanorods resulted from syntheses performed in the presence of SDS over the range of concentrations from 1.0 mM to 100 mM (Figure S7), but the DLS results indicated that there was no correlation between the dimensions of the nanorods and the dimensions of the micellar templates over the same range of concentrations (Figure S10). These results suggest that the surfactants are interacting with the surfaces of the nanocrystals and nanorods during their formation, but are not serving as templates to guide the formation of the nanorods. The outcome of this analysis further supports the suggestion that the nanorods are formed by a process of oriented attachment.

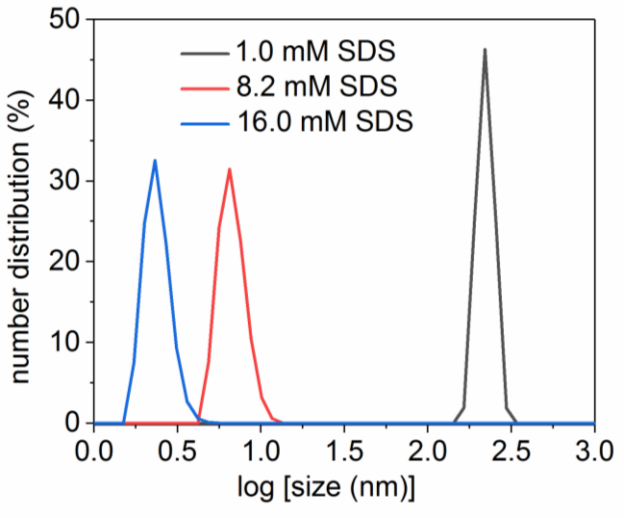

Figure S10. Dynamic light scattering (DLS) analyses of aqueous solutions containing different concentrations of SDS above its CMC value (16 mM), at the CMC value of SDS (8.2 mM), and below the CMC value of SDS (1 mM). These DLS plots display the results for the number distribution measurements using a log scale for the measured dimensions.

References

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