Supporting Information

From 1D to 3D – Macroscopic Nanowire Aerogel Monoliths

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Experimental

Chemicals

All of the following chemicals were used without further purifications: benzyl alcohol (anhydrous 99.8%, Aldrich), oleylamine (70%, Aldrich), WCl₆ (99.9%, Aldrich), chloroform (99.8%, Aldrich), ethanol (absolute, 99.8%, Fluka), liquid carbon dioxide (99.9%, PanGas AG, Switzerland), nitrogen (99.999%, PanGas AG, Switzerland), krypton (99.999%, and PanGas AG, Switzerland).

Synthesis of ultrathin tungsten oxide nanowires

Ultrathin tungsten oxide nanowires were synthesized by modifying a previously reported approach. In a typical synthesis, 200 mg WCl₆ was added to 15 ml benzyl alcohol under magnetic stirring. After the solution became blue, 0.25 ml oleylamine was added. After stirring for another 30 min, the solution was transferred to a 45 ml Teflon container with a glass tube inside, which was then sealed in a stainless steel autoclave (Parr, Acid Digestion Vessel 4744). The autoclave was heated in an oven at 180 °C for 24 h. When the oven was cooled down to room temperature, the blue precipitate was collected by centrifugation. The sample was washed with chloroform, acetone, and ethanol for several times.
Assembly of ultrathin tungsten oxide nanowires into the aerogel monolith

The freshly synthesized and wet tungsten oxide nanowires from the previous step were dispersed in 20 ml absolute ethanol (Figure. S2a). Then, the nanowire suspension was centrifuged with a speed of 4000 rpm for 5 min. After centrifugation, a blue gel-like sample formed at the bottom of the centrifuge tube (Figure S2b and c). After decanting the ethanol, 10 ml chloroform was slowly added to the centrifuge tube, upon which the gel with the shape of the bottom of the centrifuge tube floated on the chloroform (Figure S2d). The wet gel was then carefully transferred to a glass bottle filled with absolute ethanol and left there overnight to completely fill the pores with ethanol. The wet gel was supercritically dried with CO₂ in a Leica Critical Point Dryer 030.

Preparation of the tungsten oxide nanowire xerogel

After centrifugation of the nanowire suspension, the ethanol was decanted off. The blue gel-like sample together with the centrifuge tube was placed in an oven for drying at 60 °C for 12 h.

Characterization

X-ray powder diffraction (XRD) patterns were recorded on a X’Pert Pro (PANalytical B.V., Netherlands) powder diffractometer operating in reflection mode and equipped with Cu Kα radiation (45 kV, 40 mA). Transmission electron microscopy (TEM) images were obtained on a Philips CM12 (100 kV). Scanning electron microscopy (SEM) images were acquired on a Hitachi SU-70 (5 kV). Nitrogen gas sorption analysis was carried out on a Quantachrome Autosorb iQ at 77 K. Prior to the measurements, the samples were outgassed at 120 °C for 24 h. The surface area was determined via Brunauer-Emmett-Teller (BET) method and the pore size distribution and total pore volume were calculated by a density functional theory (DFT) analysis using a Non Local DFT (NLDFT) calculation model for nitrogen at 77 K based on cylindrical pores in silica.
**Figure S1.** TEM images at different magnifications of the as-synthesized ultrathin tungsten oxide nanowires.

**Figure S2.** Illustration of the different steps leading to the wet $W_{18}O_{49}$ nanowire gel. a) Dispersion of $W_{18}O_{49}$ nanowires in ethanol; b-c) gel-like precipitate achieved after centrifugation; d) monolithic wet gel floating on the solvent after addition of chloroform.
Figure S3. a-d) SEM images and e-j) TEM images of the tungsten oxide nanowire xerogel obtained by drying the wet gel in an oven at 60 °C.