Supporting Information

Polymer-mediated metallophilic interactions for gram-scale production, high-yield (~90%) synthesis of ultrathin bismuth nanowires

Tzu-Lun Kao and Hsing-Yu Tuan*

Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan 300.

AUTHOR EMAIL ADDRESS: toms00280@hotmail.com

* Corresponding author

Phone: (886)3-571-5131 ext. 42509

Email: hytuan@che.nthu.edu.
**Materials**

All chemicals were used as received without any further purification, including bismuth(III) 2-ethylhexanoate ($\text{C}_{24}\text{H}_{45}\text{BiO}_6$) from Alfa Aesar, oleylamine (OLA, 97%) from Acros Organics, trioctylamine (TOA, 98%) from Sigma-Aldrich, gold(III) chloride trihydrate ($\geq 99.9\%$) from Sigma-Aldrich, and polyvinylpyrrolidone/hexadecane (PVP-HDE) from ISP. Toluene (ACS reagent, 99.5%) and ethanol (absolute, 99.8%) for the centrifugation or dispersion were also purchased from Sigma-Aldrich.

**Characterization**

Ultrathin bismuth nanowires were characterized by the following instruments, including scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffractometer (XRD), and X-ray photoelectron spectroscope (XPS). TEM images were obtained on JEOL JEM-1200 at an accelerating voltage of 120 kV for low resolution images and on a JEOL JEM-3000F at an accelerating voltage of 300 kV, respectively. SEM images were obtained on JSM-6500. XRD data were obtained by Rigaku Ultima IV X-ray diffractometer using a Cu radiation source ($\lambda=1.54 \text{ Å}$). XPS analysis was performed on ULVAC-PHI XPS.
**Synthesis of ultrathin bismuth nanowire in heating-up style**

In a typical synthesis of ultrathin bismuth nanowires in heating-up style, 0.6386 g $\text{C}_{24}\text{H}_{45}\text{BiO}_6$, 2 g PVP-HDE, and 10 ml oleylamine (OLA) were added into a 50 ml three-necked flask inside a glovebox with both water and oxygen $<$0.1 ppm, and the flask was then sealed with a stopcock valve at the middle neck for the input of argon and with a glass tube for the temperature sensor and a rubber septum at two side necks before taken out from the glovebox. The three-necked flask was placed on a heating mantle, connected to a Schlenk line system, and purged with continuous argon flow for 30 min to ensure an oxygen-free environment to prevent the oxidization of bismuth in the heating process. The mixture was then rapidly heated to 200 °C and kept at 200 °C for 30 min with vigorous stirring. The heating mantle was then removed, and the flask was cooled down with a cool water bath, followed by the addition of 10 ml toluene and 15 ml methanol to the flask. The product was washed by centrifugation at 6000 rpm for 5 min several times. The supernatant was discarded to obtain purified ultrathin bismuth nanowires, which was stored dry under argon prior to characterization. For the large-scale production of Bi ultrathin nanowires, all the reactants are 50 times in volume and gram as the recipe shown above with a 1 L three-necked flask.
Gram-scale synthesis of ultrathin bismuth nanowire in heating-up style

31.93 g C$_{24}$H$_{45}$BiO$_6$, 5 g PVP-HDE, and 500 ml oleylamine (OLA) were added into a 1 liter three-necked flask inside a glovebox with both water and oxygen <0.1 ppm, and the flask was then sealed with a stopcock valve at the middle neck for the input of argon and with a glass tube for the temperature sensor and a rubber septum at two side necks before taken out from the glovebox. The three-necked flask was placed on a heating mantle, connected to a Schlenk line system, and purged with continuous argon flow for 30 min. The mixture was then rapidly heated to 200 °C and kept at 200 °C for 1 day with vigorous stirring. The heating mantle was then removed, and the flask was cooled down with a cool water bath. The resulting product was purified by centrifugation at 6000 rpm for 5 min several times. The supernatant was discarded to obtain purified ultrathin bismuth nanowires, which was stored dry under argon prior to characterization.
Figure S1 (a-e) SEM images of as-synthesized Bi UNWs at various magnifications.
Figure S2 TEM image of as-synthesized Bi UNWs.
Figure S3 (a) XRD spectrum of the as-synthesized Bi UNWs (b) simulated unit cell of bismuth based on the XRD result.

Figure S4 TEM images of Bi UNWs (a) before e-beam irradiation (b) after e-beam irradiation. (c-d) TEM images of melted Bi UNWs bundle and the resulting liquid droplets on the wire surface with constantly varying crystallinity.
Figure S5 TEM image of as-synthesized Bi UNWs with the diameter of some UNWs measured in nm.
Figure S6  (a-f) TEM images of as-synthesized Bi UNWs with the scale bar equivalent to 5 nm.
Figure S7 XRD spectrum of Au\(^+\) complex gel prepared by continuously stirring the mixture of 0.2 mmol gold(III) chloride trihydrate and 20 ml oleylamine at room temperature for 2 days.\(^1\)

Figure S8 TEM images with a scale bar of 1 μm of the resulting product obtained from the synthesis (a) at room temperature for 1 day (b) at 200 °C for 30 min (c) at 250 °C for 30 min.
Figure S9 TEM images of the corresponding product resulted from the synthesis using (a) oleylamine (b) trioctylamine as the reducing agent at 200 °C for 30 minutes.

Figure S10 XRD spectrum of the as-synthesized Bi UNWs in gram-scale synthesis.
References