Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

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

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Materials

All chemicals were used as received without any further purification, including bismuth(III) 2-ethylhexanoate ($C_{24}H_{45}BiO_6$) from Alfa Aesar, oleylamine (OLA, 97%) from Acros Organics, trioctylamine (TOA, 98%) from Sigma-Aldrich, gold(III) chloride trihydrate (≥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 (λ= 1.54 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 $C_{24}H_{45}BiO_6$, 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.

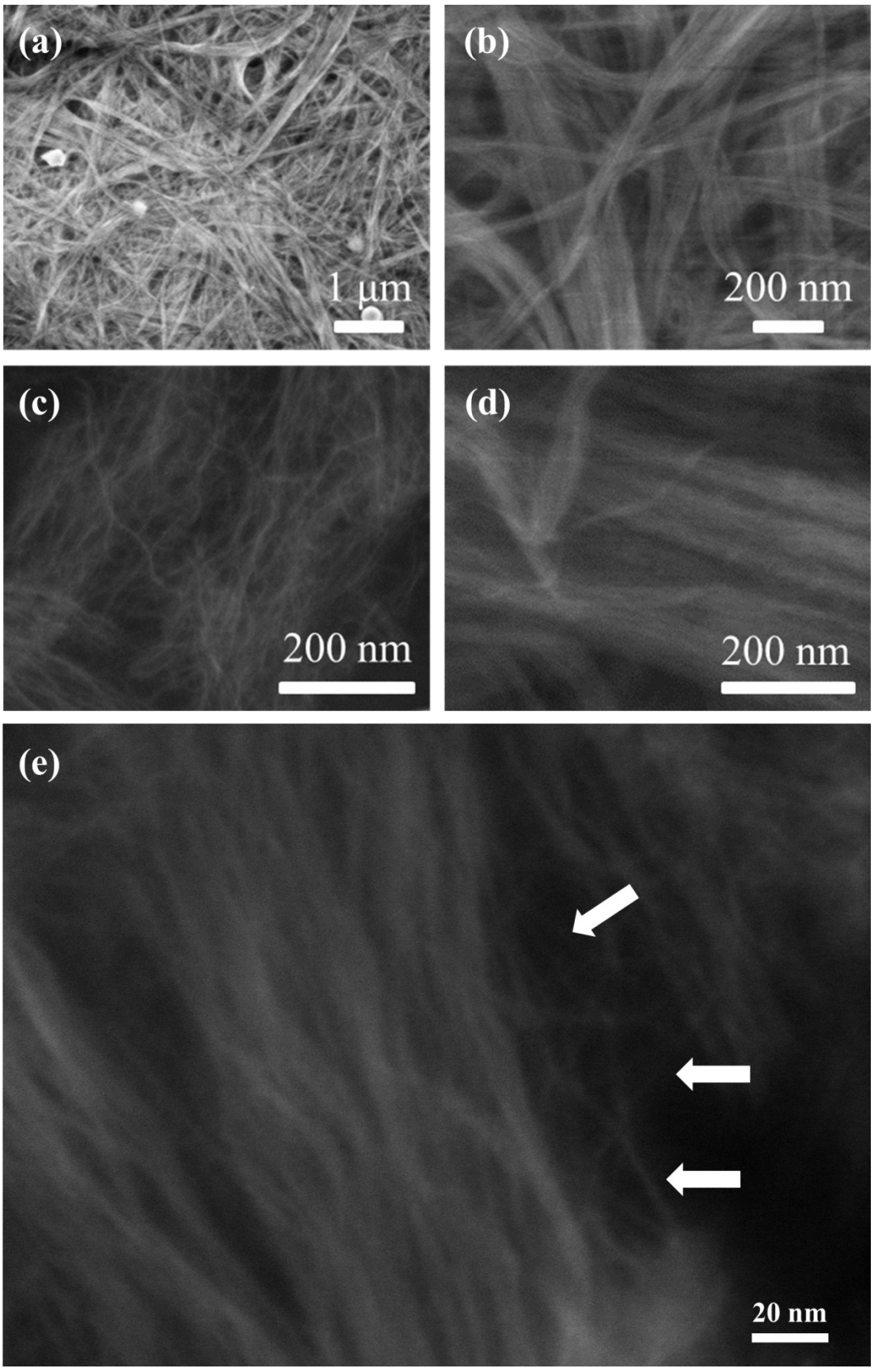

Figure S1 (a-e) SEM images of as-synthesized Bi UNWs at various magnifications.

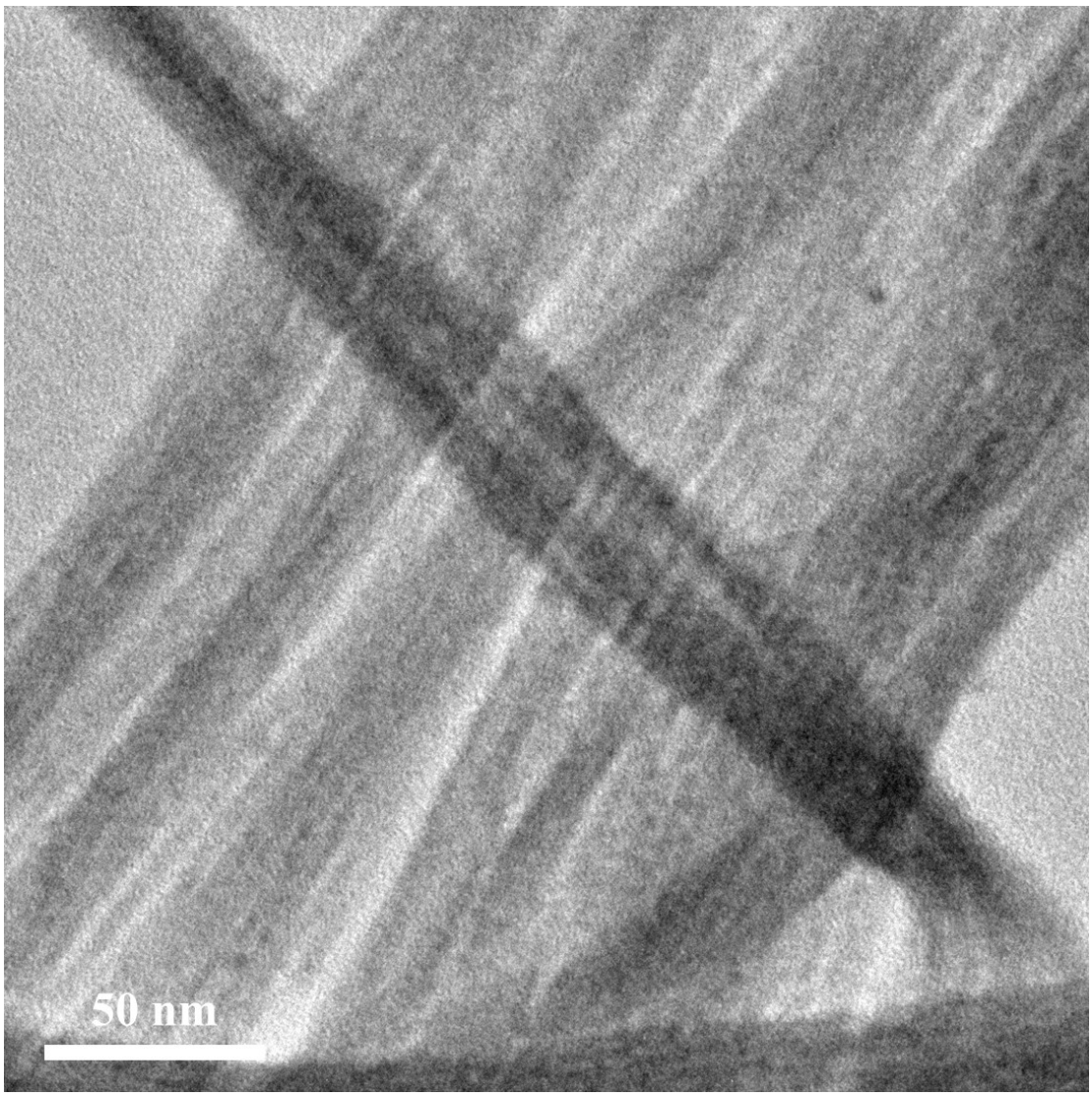

Figure S2 TEM image of as-synthesized Bi UNWs.

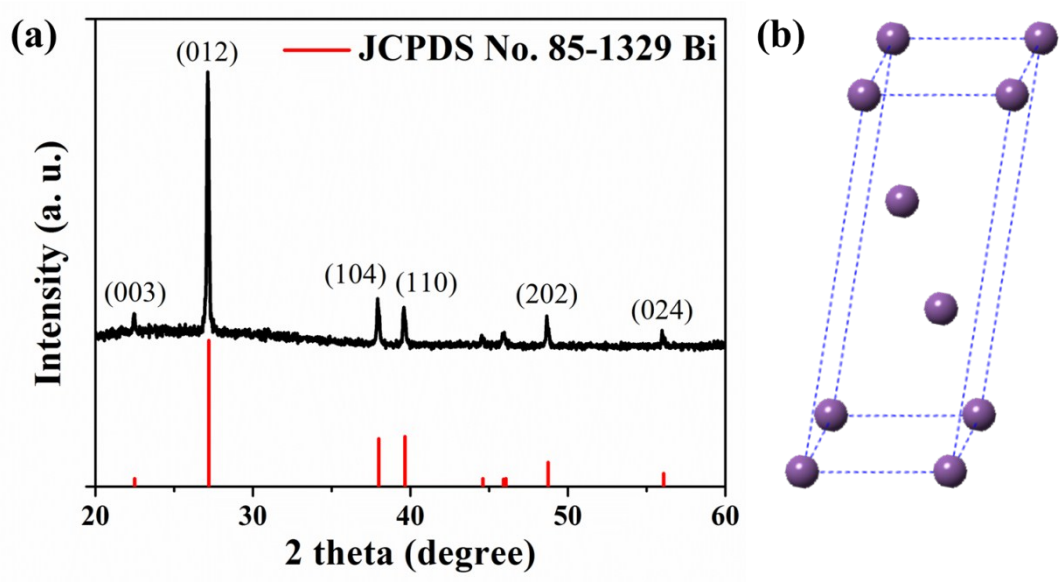

Figure S3 (a) XRD spectrum of the as-synthesized Bi UNWs (b) simulated unit cell of bismuth based on the XRD result.

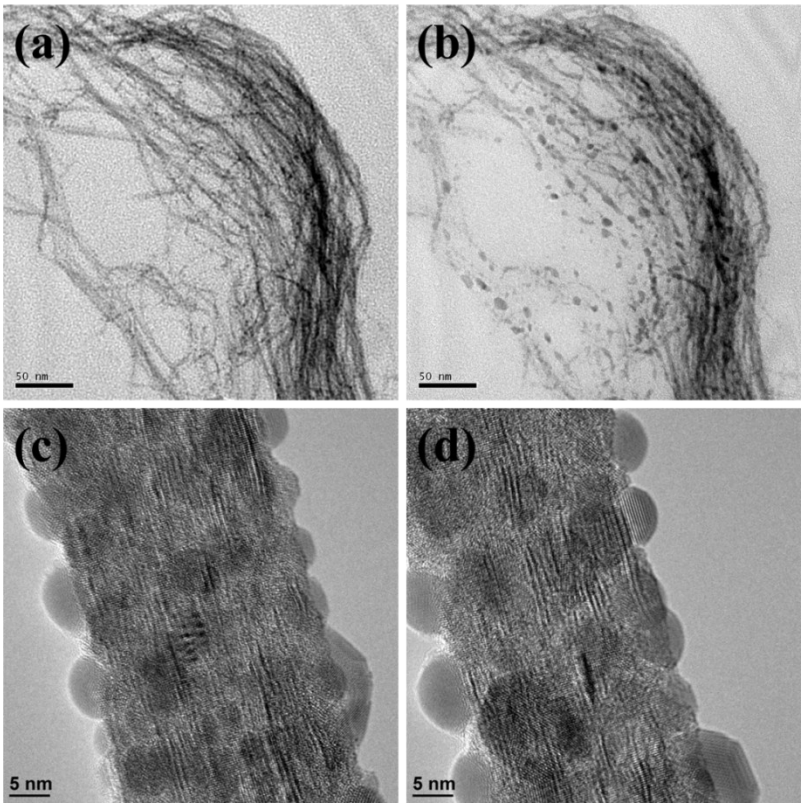

Figure S4 TEM images of Bi UNWs (a) before e-beam irradiation (b) after e-beam irradiation. (c-d) TEM images of melted Bi UNWs bundle and the resulting liquid droplets on the wire surface with constantly varying crystallinity.

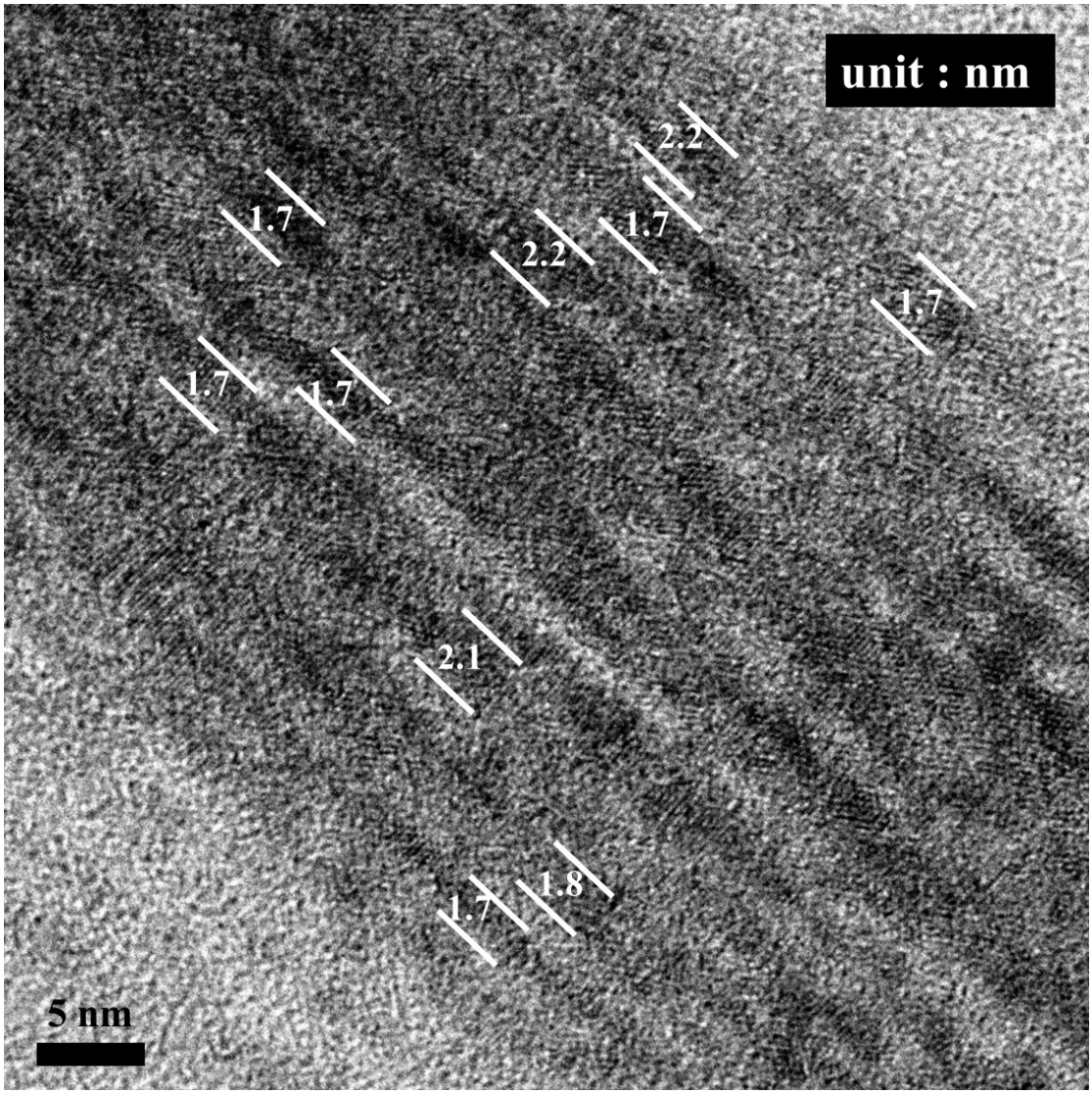

Figure S5 TEM image of as-synthesized Bi UNWs with the diameter of some UNWs measured in nm.

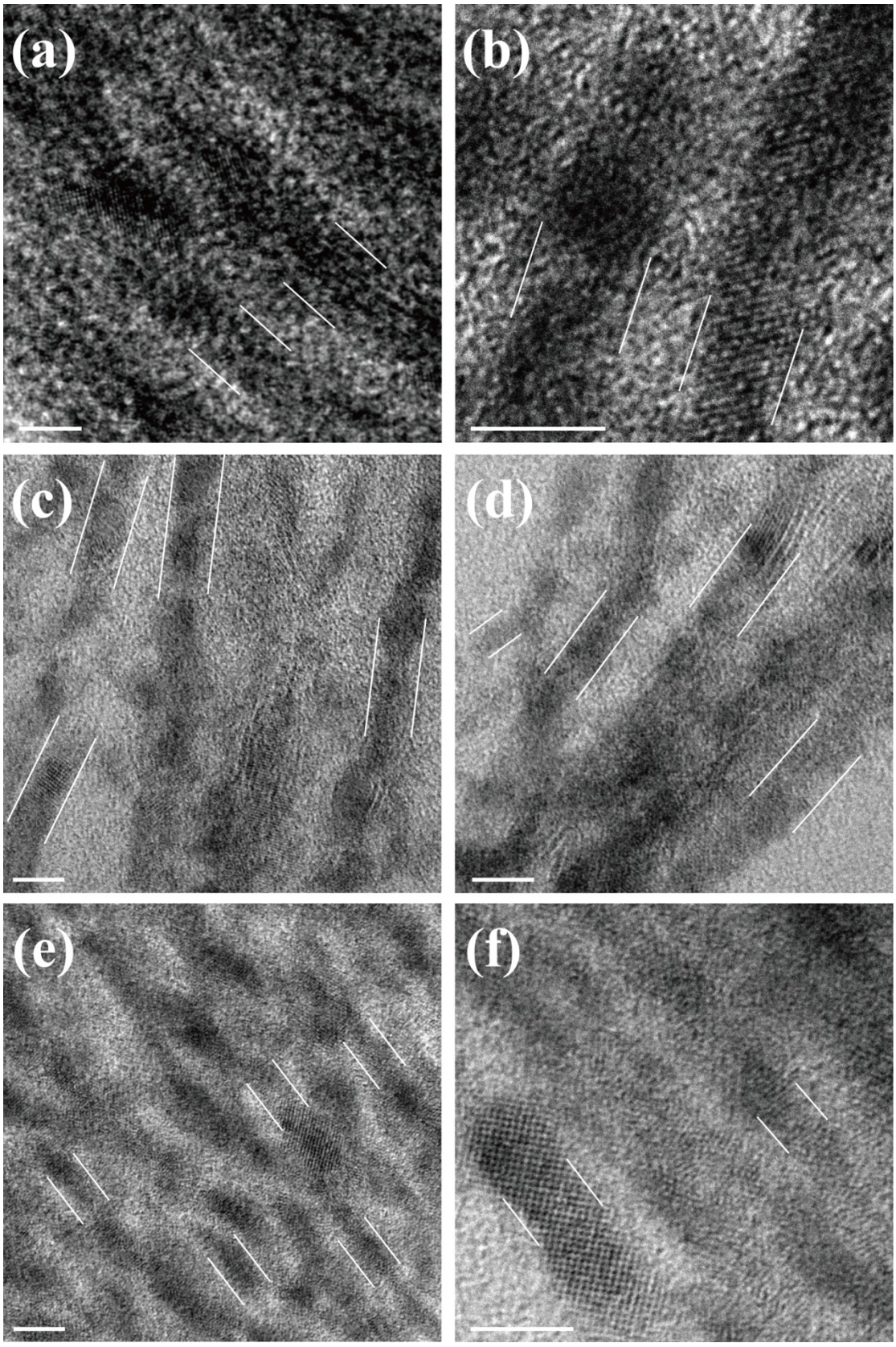

Figure S6 (a-f) TEM images of as-synthesized Bi UNWs with the scale bar equivalent to 5 nm.

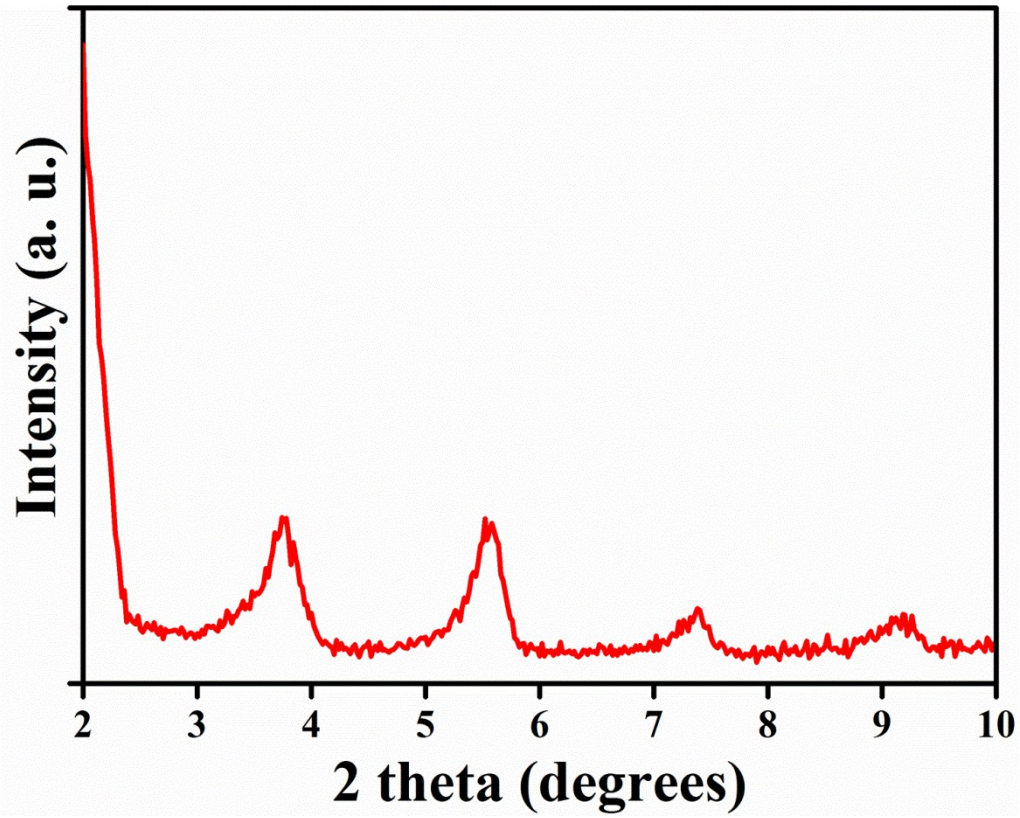

Figure S7 XRD spectrum of Au^{+} complex gel prepared by continuously stirring the mixture of 0.2 mmol gold(III) chloride trihydrate and 20 ml oleylamine at room temperature for 2 days.[1]

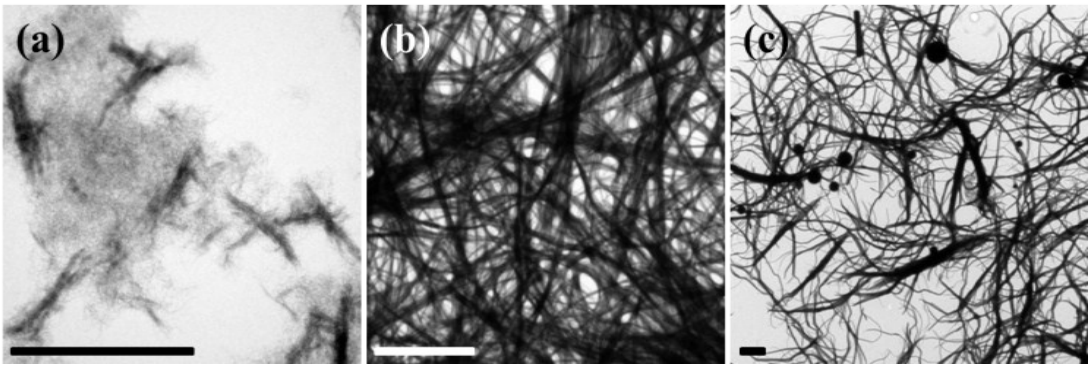

Figure S8 TEM images with a scale bar of 1 μm of the resulting product obtained from the synthesis (a) at room temperature for 1 day (b) at 200 °C for 30 min (c) at 250 °C for 30 min.

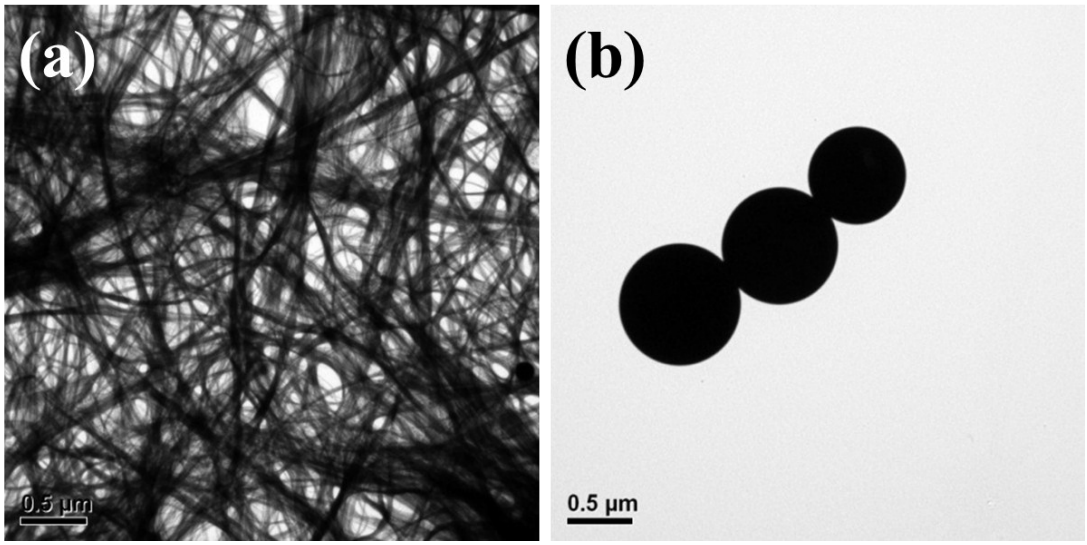

Figure S9 TEM images of the corresponding product resulted from the synthesis using (a) oleylamine (b) trioctylamine as the reducing agent at 200 ° C for 30 minutes.

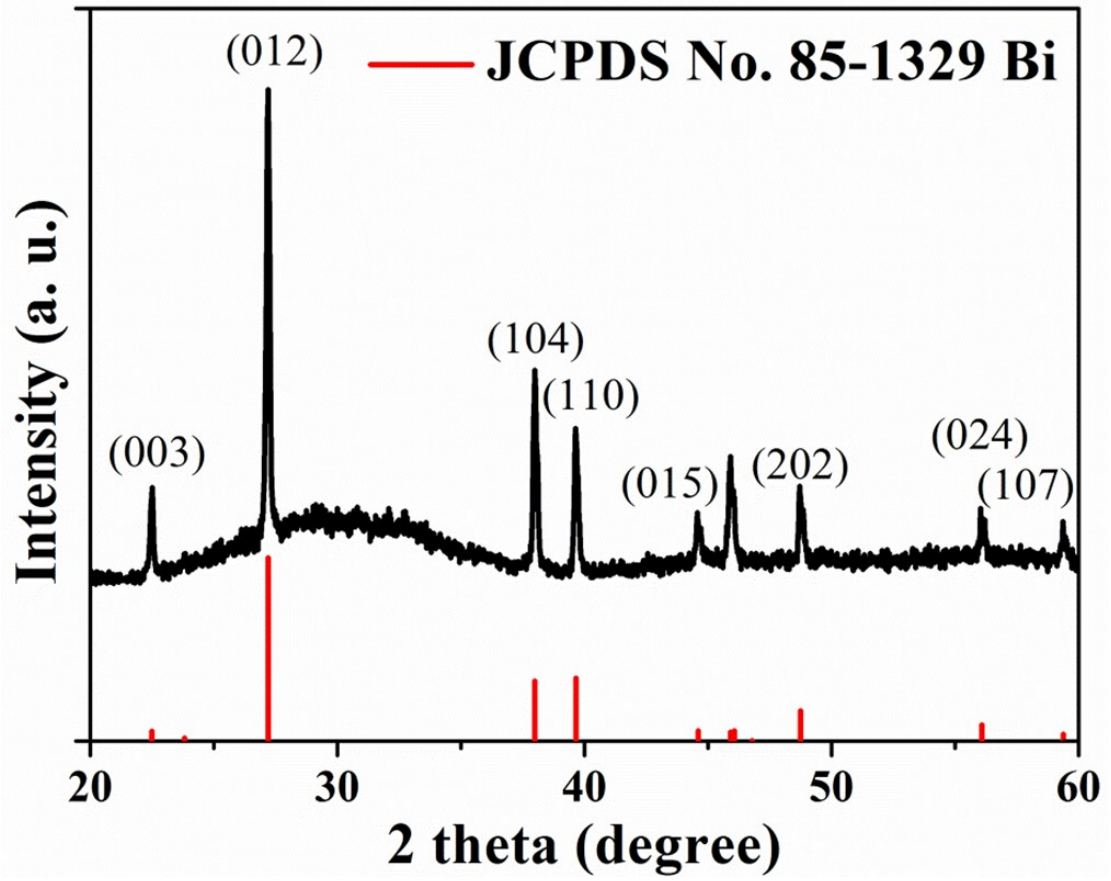

Figure S10 XRD spectrum of the as-synthesized Bi UNWs in gram-scale synthesis.

References

1. Z. Huo, C.-k. Tsung, W. Huang, X. Zhang, and P. Yang, *Nano Lett.*, 2008, **8**, 2041-2044.