Electrochemical synthesis of metal and semimetal nanotube–nanowire heterojunctions and their electronic transport properties†

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Metal and semimetal nanotube–nanowire heterojunction arrays have been achieved by sequential electrochemical-deposition inside the nanochannels of anodic aluminium oxide template with a layer of Au thin enough to leave the pores open.

Heterojunctions of one-dimensional nanostructures have received considerable attention due to their unique properties,[1–3] and potential applications in nanodevices.[4–8] Previous studies on longitudinally segmented heteronanostructures have mainly focused on two segments of nanowires (NWs),[9–12] two segments of nanotubes (NTs),[13] and one segment of NTs and another segment of NWs.[14–17] For NT–NW heterostructures, the NT segments are usually carbon NTs, which have been prepared by catalytic growth,[14] chemical vapor deposition,[15] solid–solid reaction,[16] and surface attaching methods.[17] However, little has been reported on nanoheterojunctions with one longitudinal segment consisting of metallic or semimetal NTs, which might have potential applications in future nanotechnology.

Here, we demonstrate a facile approach for the building of metal and semimetal nanotube–nanowire (NT–NW) nanoheterojunction arrays by sequential electrochemical deposition of two materials inside the nanochannels of anodic aluminium oxide (AAO) template. Herein we take metal Cu and semimetal Bi as examples. The heterojunction arrays of Cu NTs and Bi NWs (CuNT–BiNW) are achieved by electrochemical deposition of Cu first, and then Bi in the nanochannels of the AAO template with one side coated with an Au layer which is thin enough to leave the pores open and cover only the top surface of the pore walls, as is shown schematically in the ESI.† Similarly, if the electrodeposition sequence is changed to Bi first and then Cu, in this case heterojunction arrays of Bi NTs and Cu NWs (BiNT–CuNW) can be achieved (see ESI†).

As for the CuNT–BiNW heterojunction arrays, Fig. 1(a) and (b) reveal the SEM images of the BiNWs segment and the CuNTs segment, respectively, after the template was partially removed. Both the CuNTs and the BiNWs have an outer diameter about 80 nm, in agreement with that of the nanochannels in the AAO template. Fig. 1(c) shows a side-view SEM image of a bundle of CuNT–BiNW heterojunctions after the AAO template was completely removed. The three dashed circles marked I, II and III are the BiNWs segment, junction area and CuNTs segment, respectively, which have been further confirmed by the corresponding EDS analyses shown in Fig. 1(d), (e) and (f), respectively. It can be seen that the CuNTs (marked by dashed circle III) are quite uniform with smooth surface, while the BiNWs (dashed circle I) are not so uniform with rough surface.

The diameters of the nanochannels inside the AAO templates can be adjusted through modulating the applied anodizing voltage and subsequent pore widening, and the length of the nanochannels can be controlled by the anodization time, while the lengths of the CuNT and the BiNW segments inside the nanochannels can be adjusted by the corresponding electrodeposition parameters. Therefore, the diameter and the relative length of the CuNT and BiNW segments can be modulated as designed.

In order to identify the top structure of the CuNT segments, we electrodeposited one sample with only CuNTs inside the half depth of the nanochannels. After template removal, SEM observation

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Fig. 1 (a) Top-view SEM image of BiNWs segment. (b) Bottom-view SEM image of CuNTs segment. (c) Side-view SEM image of CuNT–BiNW heterojunction arrays, the inset is a close-up view of the marked rectangular region. (d)–(f) EDS spectra from the corresponding regions I, II, III marked in (c).

Fig. 2 (a) SEM image of the electrodeposited CuNTs with closed caps, broken CuNTs and CuNT roots. (b) TEM image of CuNT–BiNW heterojunction, the inset SAED patterns on the upper-right and lower-left corners are taken from the marked areas of I and II, respectively.

(Fig. 2(a)) reveals that the CuNTs have closed caps on top, on which BiNWs will be deposited in the subsequent electrodeposition of Bi. The caps formed on top of CuNTs may be ascribed to the overpotential, leading to the remnant electrolyte to form a thin Cu layer covering the opening of the CuNTs on top, after the power supply is shut off, while underpotential electrochemical deposition is favorable to obtain even or uniform NTs.[13]

In our experiments, the formation of the CuNTs depends on two factors. The first factor is gold-sputtering.[18] By decreasing the sputtering duration, a very thin gold layer is sputtered to cover only the top surface of the nanochannel walls and leave the pores still open. Accordingly, the electrodeposition of the CuNTs initiates from the circular edges of the nanochannels on the Au-coated side, then grow around the channel walls and along the channel axial direction. Under the channel space confinement the CuNTs are formed. Moreover, our experiments suggest that the metallic caps on top of the tubes are independent of the NT length and the thickness of sputtered gold layer if the layer is thin enough to electrodeposit nanotubes. The second factor is the electrodeposition parameters. During the electrodeposition, we tried various current densities, and found that when the optimal current density was in the range of 1.8–2.7 mA cm^{-2},[13,18,19] CuNTs with caps on top could be formed. Otherwise CuNWs or uneven CuNTs would be formed.[13,20]

In order to identify the tubular structure and observe the heterojunction area clearly, we synthesized a CuNT–BiNW heterojunction sample with the walls of CuNTs segment being much thinner (more data and analysis about the controlling crystallization of NT–NW heterojunctions is provided in the ESI†). One CuNT–BiNW heterojunction is shown in Fig. 2(b), and the light contrast segment (marked by dashed circle I) and the dark contrast segment (circle II) are CuNT and BiNW, respectively. The wall thickness of the CuNTs is about 10 nm. The SAED patterns on the upper-right and lower-left corners are taken from the corresponding CuNT and BiNW segments, respectively, indicating that the CuNT is polycrystalline, while the BiNW is single-crystalline.

Since the CuNT segment with thinner walls is usually polycrystalline (see Fig. 2(b)), in order to observe the heterojunction interface between CuNTs and BiNWs, we have synthesized a sample in which both the CuNT and BiNW segments are single-crystalline (Fig. 3(c)) by controlling the parameters of the sputtered gold layer and electrodepositing parameters. As a result of modulating the electrodepositing parameters during the electrodeposition process, the growth status changed accordingly, leading to different strong diffractive peaks in the two corresponding XRD spectra taken from the CuNT (Fig. 3(a)) and BiNW (Fig. 3(b)) segment sides, respectively. Fig. 3(c) is a TEM image of a BiNW segment of a CuNT–BiNW heterojunction. The dark and light contrast segments correspond to CuNTs and BiNWs respectively, and the CuNTs have a wall-thickness about 20 nm. A HRTEM image taken from the dashed rectangle in Fig. 3(c) displays the interface between the CuNT and BiNW segments. Because the Cu orientation of zone axes cannot be controlled at present – the lattice spacing of Cu is small (the maximum interplane spacing of

Fig. 3 (a), (b) XRD patterns taken from the BiNW and CuNT segments, respectively. (c) a TEM image of CuNT–BiNW heterojunction with corresponding SAED patterns (the SAED pattern in the junction region, the spots of Bi are marked " × "). (d) HRTEM image of the heterojunction taken from the dashed rectangle of (c).

Cu(111) planes is 2.08 Å, while our HRTEM resolution is 1.9 Å), and the wall of single-crystalline CuNTs are usually thick, therefore the HRTEM image is blurred. The SAED patterns in Fig. 3(c) are taken from rhombohedral Bi and face-centered Cu, respectively. From the SAED patterns, it can be seen that the preferred growth directions of BiNWs and CuNTs are close to [101] and [111] orientations, and that the zone axes of CuNTs and BiNWs are [0$\bar{1}$1] and [0$\bar{1}$0], respectively. The pattern (Fig. 3(c)) and lattice-resolved image (Fig. 3(d))taken from the junction region between the BiNW and CuNT segments show that the Bi (10$\bar{2}$) plane (marked with ×) is nearly parallel to the Cu(200) plane, but there is still an angle of about 2° between the two planes. As a result, it can not be judged what the relation is between Cu(200) plane and the Bi(01$\bar{2}$) plane at the junction region. A HRTEM image of the BiNT–CuNW junction area and the description are provided in the ESI.†

In order to evaluate the electronic transport difference of the two types of heterojunctions, we measured their I–V curves. Fig. 4(a) shows the I–V curve of the CuNT–BiNW heterojunction arrays, revealing linear and symmetrical characteristics. However the I–V curves of BiNT–CuNW heterojunction arrays (Fig. 4(b)) are nonlinear. Previous studies have revealed that bismuth is a semimetal, and BiNWs can be either metallic (with diameters larger than 70 nm) or semiconducting (with diameters about 50 nm or smaller), depending on their diameters.[21,22] In our experiments, BiNW segments are about 80 nm in diameter, larger than the critical value (65 nm) of the semimetal–semiconductor transition,[23] and therefore show metallic properties. Because Cu nanotubes are always metallic, our CuNT–BiNW heterojunction arrays show metal–metal junction behavior. Recent experimental results of R–T curves on BiNTs indicated that a semimetal–semiconductor transition occurs as the BiNT wall thickness decreases from 100 to 15 nm and independent of the diameters, is determined by the quantum confinement effect.[24] In our BiNT–CuNW heherojunction arrays, the BiNT segments with wall thickness about 20 nm and diameter about 80 nm have undergone a semimetal–semiconductor transition, showing semiconductor behavior, while the CuNW segments are always metallic. So the BiNT–CuNW heterojunction arrays show metal–semiconductor junction behavior.

In summary, we have demonstrated a simple approach to prepare heterojunction arrays of NTs and NWs of metal Cu and semimetal Bi by sequential electrodeposition of the two materials inside the nanochannels of an AAO template with an Au layer thin enough to leave the pores open. The I–V curve measurements reveal that CuNT–BiNW heterojunction arrays are metal–metal junctions, while the BiNT–CuNW heterojunction arrays show metal–semiconductor electronic transport behavior. Our method might be exploited to synthesize NT–NW heterojunctions of other electrodeposited materials for future nanotechnology.

Fig. 4 I–V curves of CuNT–BiNW (a) and BiNT–CuNW (b) heterojunctions at various temperatures.

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