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## Cu<sub>3</sub>N/Cu<sub>2</sub>O core–shell nanowires: growth and properties†

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CuO nanowires with diameters between 100 and 200 nm, lengths up to ~10 μm and a uniform distribution have been grown at 600 °C under 100 mL min<sup>-1</sup> O<sub>2</sub> on 15 mm × 30 mm Cu foils. The CuO nanowires have a monoclinic crystal structure, grow by a vapor–solid mechanism and can be reduced to Cu under H<sub>2</sub> at 300 °C but they are shortened, contain residual Cu<sub>2</sub>O and are eliminated above 400 °C. We develop a strategy to preserve their integrity via the deposition of Cu over the CuO in order to convert them into Cu<sub>3</sub>N under NH<sub>3</sub>:H<sub>2</sub>. The Cu<sub>3</sub>N nanowires obtained in this way are curly and have a cubic anti-ReO<sub>3</sub> crystal structure but are surrounded by a surface shell of Cu<sub>2</sub>O with a thickness of a few tens of nm as shown by transmission electron microscopy. We find that the CuO NWs coated with Cu having a thickness greater than 200 nm are not fully converted into Cu<sub>3</sub>N and have an inner core of CuO. The Cu<sub>3</sub>N nanowires exhibited four maxima in differential transmission at 2.41, 2.17, 1.9 and 1.8 eV, using ultrafast absorption–transmission spectroscopy, corresponding to the M and R direct energy band gaps of Cu<sub>3</sub>N in good agreement with theory but we find no evidence for quantization. In addition, we observed two minor peaks at 1.69 and 1.67 eV that may be related to transitions between states in the Cu<sub>2</sub>O shell or Cu<sub>3</sub>N under compression. Despite the fact that Cu<sub>3</sub>N has no mid-gap states the photo-generated carriers have lifetimes less than 100 ps, so its potential as a defect tolerant semiconductor for energy conversion is discussed along with its perspective for energy storage.

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### 1. Introduction

Cu<sub>3</sub>N<sup>1</sup> is a binary semiconductor with an indirect energy band gap of 1.0 eV that has a cubic a-ReO<sub>3</sub> crystal structure with a lattice constant of 3.8 Å (space group *PM3m*, Number 221).<sup>2</sup> It has been described as a defect tolerant semiconductor which is the tendency of a semiconductor to keep its properties despite the presence of crystallographic defects as suggested by Zakutayev *et al.*<sup>3</sup> As such it has been proposed to be used as a solar cell absorber considering that bipolar doping is possible<sup>3</sup> but also for energy storage and the realization of batteries<sup>4</sup> due to the large voids in the center of its cubic structure that can accommodate foreign atoms, such as lithium.<sup>5</sup> It has been found that Li<sub>3-x</sub>Cu<sub>x</sub>N has a high reversible capacity of 650 mA h g<sup>-1</sup> so Cu<sub>3</sub>N is indeed an attractive material for energy storage and Lithium-ion

batteries (LIB)<sup>6,7</sup> but so far no one has fabricated a solar cell device using Cu<sub>3</sub>N exhibiting photovoltaic action.

In the past, Cu<sub>3</sub>N layers have been prepared by a variety of methods including, sputtering,<sup>8</sup> molecular beam epitaxy,<sup>9</sup> atomic layer deposition<sup>10,11</sup> and pulsed laser deposition<sup>12,13</sup> but in most cases Cu<sub>3</sub>N has been obtained by sputtering under Ar and N<sub>2</sub>. For instance, Birkett *et al.*<sup>8</sup> prepared Cu<sub>3</sub>N by sputtering under Ar and N<sub>2</sub> and the direct energy band gap was found to be 1.68 eV at 300 K which increased very slightly up to 1.7 eV at 4.2 K consistent with their electronic structure calculations. Recently, Matsuzaki *et al.*<sup>14</sup> obtained Cu<sub>3</sub>N directly from Cu under NH<sub>3</sub> and O<sub>2</sub> at temperatures ranging between 500 °C and 800 °C. The conversion of Cu into Cu<sub>3</sub>N was suggested to occur *via* a two-step reaction of Cu with O<sub>2</sub> and then with NH<sub>3</sub> which in a way is similar to the conversion of Ga<sub>2</sub>O<sub>3</sub> nanowires into GaN under NH<sub>3</sub> at elevated temperatures.<sup>15</sup>

In the past only, a few have investigated the growth and properties of Cu<sub>3</sub>N nanowires (NWs). More specifically Wang *et al.*<sup>16</sup> prepared Cu<sub>3</sub>N NWs by forming Cu(OH)<sub>2</sub> NWs on Cu foils that were subsequently exposed to NH<sub>3</sub> at 350 °C for 3 h. In addition, Ma *et al.*<sup>17</sup> observed the formation of a planar network of sub-nm diameter Cu<sub>3</sub>N NWs on Cu(110) foils by strain relief guided growth under N<sub>2</sub> at 10<sup>-7</sup> mbar and 427 °C. Moreover, Zhang *et al.*<sup>18</sup> obtained Cu<sub>3</sub>N rods by metal organic chemical

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vapor deposition (MOCVD) using copper(II) acetylacetonate with  $\text{H}_2:\text{NH}_3$  while Hou *et al.*<sup>19</sup> investigated the electrical properties of Ni– $\text{Cu}_3\text{N}$  NWs and used them for water splitting. More recently,  $\text{Cu}_3\text{N}$  NWs were prepared by the formation of  $\text{Cu}(\text{OH})_2$  NWs on Cu foils after which they were converted into  $\text{Cu}_3\text{N}$  under a flow of  $\text{NH}_3$ . Following this,  $\text{Li}_3\text{N}/\text{Cu}$  NWs were obtained by bringing the  $\text{Cu}_3\text{N}$  NWs into contact with Li.<sup>20</sup> Lastly,  $\text{Cu}_3\text{N}$  NWs have also been obtained *via* an ammonolysis reaction of copper oxide films.<sup>21</sup>

Here, we have investigated the growth and conversion of CuO into  $\text{Cu}_3\text{N}$  NWs. CuO NWs have been obtained in the past mainly *via* the thermal oxidation of Cu in air or under  $\text{O}_2$  due to the inherent simplicity of this method.<sup>22</sup> Interestingly, a detailed investigation into the growth of CuO NWs on different Cu surfaces was carried out recently by Popovski *et al.*<sup>23</sup> confirming that CuO NWs may be obtained on Cu foils at temperatures as low as 250 °C. The growth of CuO NWs on Cu foils has also been achieved at low temperatures between 250 °C and 450 °C by Gulbransen *et al.*<sup>24</sup> On the other hand, it has been shown by Liang *et al.*<sup>25</sup> that the growth of CuO NWs depends on the annealing temperature and the grain size of the Cu foil that is used as substrate. A smaller grain size and single grain orientation can produce longer, denser and a more uniform distribution of CuO NWs. However, a significant disadvantage of the CuO NWs obtained *via* the thermal oxidation of Cu foils is that intermediate layers of CuO and  $\text{Cu}_2\text{O}$  are formed so a significant lattice mismatch exists between the Cu, CuO and  $\text{Cu}_2\text{O}$  which in turn makes the CuO NW network particularly fragile. Nevertheless, it has been shown that the integrity of the CuO NWs can be improved by texturing the surface of the Cu foil.<sup>26</sup> It is interesting to point out here that CuO NWs have been used in dye sensitized solar cells,<sup>27</sup> sensors,<sup>28–31</sup> as well as for catalysis<sup>32</sup> so the growth, properties and applications of CuO NWs is an ongoing topic of active investigation which is interesting from a fundamental and technological point of view.<sup>33</sup>

To the best of our knowledge, no one has investigated previously the conversion of CuO into  $\text{Cu}_3\text{N}$  NWs under  $\text{NH}_3:\text{H}_2$  which is similar to our earlier investigations on the conversion of  $\text{Ga}_2\text{O}_3$  into GaN NWs under  $\text{NH}_3$  at elevated temperatures.<sup>15</sup> We have investigated the structural properties of the CuO and  $\text{Cu}_3\text{N}$  NWs by X-ray diffraction, transmission and scanning electron microscopy as well as Raman spectroscopy. In addition, we have carried out ultrafast pump-probe spectroscopy (UPPS) which is a versatile tool for understanding the generation-recombination, mechanisms and pathways, of photo generated electron-holes that depend on the electronic band structure and energetic position of sub-band gap states related to crystal imperfections and impurities that can't be determined by steady state UV-vis absorption-transmission spectroscopy.

## 2. Materials and methods

Initially square foils of 10 mm × 10 mm Cu (99.9%) with a thickness of ~0.15 mm or 150 μm were immersed in a solution of HCl and De-ionized (DI)  $\text{H}_2\text{O}$  (1:1) to remove the native

oxide. Subsequently the foils were rinsed with DI water, dried with nitrogen and pressed flat. The growth of CuO NWs on the Cu foils was carried out in a 1" hot wall, horizontal, chemical vapor deposition (CVD) reactor, capable of reaching 1100 °C that was fed on the upstream side by a manifold consisting of four mass flow controllers connected to Ar,  $\text{NH}_3$ ,  $\text{O}_2$  and  $\text{H}_2$ . The Cu foil was loaded in a quartz boat that was inserted in the reactor after which it was purged with 500 mL  $\text{min}^{-1}$  of Ar for 10 min at 1 bar. Then the temperature was ramped at 10 °C  $\text{min}^{-1}$  under a flow of 300 mL  $\text{min}^{-1}$   $\text{O}_2$  up to 600 °C. Upon reaching 600 °C the same flow of  $\text{O}_2$  was maintained for 120 min. In order to prevent the development of thermal stress in the Cu foil, the cooling rate was adjusted to 5 °C  $\text{min}^{-1}$ . The conversion of CuO into  $\text{Cu}_3\text{N}$  NWs was carried out in the temperature range of 300–400 °C for 60 min under a flow of (a)  $\text{NH}_3$  (b)  $\text{NH}_3:\text{H}_2$  and (c)  $\text{NH}_3:\text{O}_2$  after purging with 500 mL  $\text{min}^{-1}$  of Ar for 10 min. In all cases the samples were removed from the reactor at room temperature.

The morphology and crystal structure of the  $\text{Cu}_3\text{N}$  NWs were determined by Scanning Electron Microscopy (SEM, TESCAN) operated at an accelerated voltage of 30 kV and X-ray diffraction (XRD, Rigaku Co) using Cu  $K_\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) with  $\theta$ - $2\theta$  mode ranging from 10 to 80°. Transmission Electron Microscopy (TEM) and high-resolution TEM (HRTEM) observations were carried out in a JEOL JEM F200 CFEG TEM/STEM electron microscope operated at 200 kV (point resolution 0.19 nm). TEM samples were prepared by mechanically rubbing the CuO and  $\text{Cu}_3\text{N}/\text{Cu}_2\text{O}$  NWs onto TEM carbon coated copper grids. Raman Spectroscopy (RS) was carried out using a DILOR-XY spectrometer equipped with an optical microscope and a 100× objective; the Raman measurements were performed in the backscattering geometry. The red line ( $\lambda = 647.1 \text{ nm}$ ) of a  $\text{Kr}^+$  laser was used for excitation and the spectra were calibrated with a Ne lamp. The power on the sample was less than 2 mW.

Finally, the optical properties of the  $\text{Cu}_3\text{N}$  NWs were investigated by measuring the time evolution of the differential transmission ( $dT/T$ ) on a ps time scale by UPPS using a pump with  $\lambda_{\text{PU}} = 400$  or 260 nm and diameter of 1 mm on the sample and a probe that was varied between  $\lambda_{\text{PR}} = 450$  nm and 750 nm. In this case the CuO NWs were removed from the Cu foil by sonication in isopropanol and dispersed gradually on fused silica ( $\text{f-SiO}_2$ ) after which they were converted into  $\text{Cu}_3\text{N}$  under  $\text{NH}_3:\text{H}_2$  at 400 °C. UPPS was carried out using a Ti: Sapphire ultrafast amplifier system generating 100 fs pulses at 800 nm and running at a repetition rate of 1 kHz. A nonlinear crystal was used to generate 400 nm for the purpose of exciting the sample, whereas part of the fundamental was used to generate a super continuum light for probing different energy states. The measurements were carried out using a typical pump-probe optical setup in a non-collinear configuration, where the probe beam was directed into a spectrometer with 0.5 nm spectra resolution equipped with a fast CCD array.

## 3. Results and discussion

### 3.1 Growth of CuO nanowires on Cu foil

In the past, we have obtained CuO NWs by the thermal oxidation of a Cu foil with a thickness of ~0.15 mm.<sup>34</sup> More specifically,



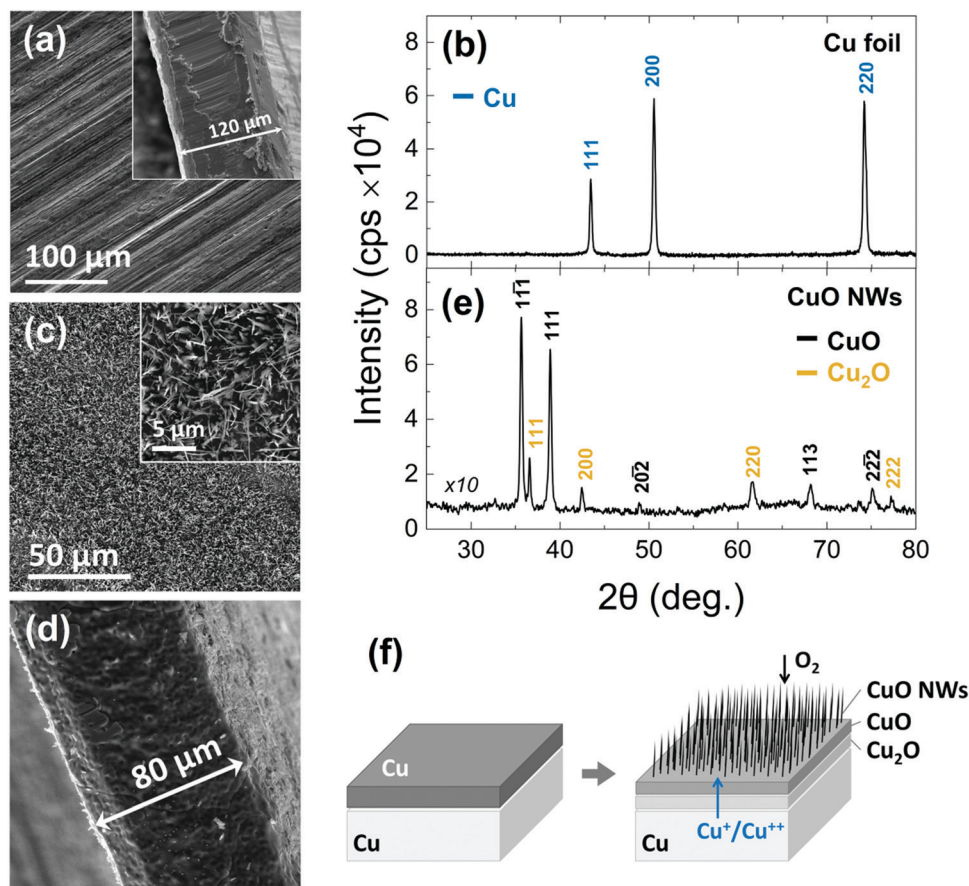
the CuO NWs were obtained in a 1" hot wall reactor that was purged with Ar for 10 min after which the temperature was ramped to 600 °C using a slow ramp rate of 5 °C min<sup>-1</sup> and a flow of 100 mL min<sup>-1</sup> O<sub>2</sub> that was maintained up to 4 h at 600 °C. The CuO NWs obtained in this way were straight with diameters of ~100 nm, had lengths of up to ~10 μm and exhibited clear peaks in the XRD corresponding to the monoclinic crystal structure of CuO but additional peaks were also observed corresponding to the underlying Cu<sub>2</sub>O and Cu foil.

Here, we have grown again CuO NWs on Cu foils at 600 °C for 120 min in order to convert them into Cu<sub>3</sub>N NWs by thermal nitridation. A typical SEM image of the Cu foils used for the growth of the CuO NWs is shown in Fig. 1(a). This exhibited well resolved peaks in the XRD as shown in Fig. 1(b) corresponding to the face centered cubic (fcc) crystal structure of Cu with a lattice constant of 3.597 Å. A cross-section of the Cu foil is also shown as an inset in Fig. 1(a), from which we find that it has a thickness of about 120 μm. The CuO NWs that were grown on the Cu foil have diameters of ~100–200 nm, lengths of ~3–10 μm and form a dark black network with excellent uniformity across areas up to 15 × 30 mm. A typical SEM image of the CuO NWs is shown in Fig. 1(c). In fact, the CuO NWs grow on top of a bilayer of bulk CuO and Cu<sub>2</sub>O over the Cu foil.

A reduction of about 40 μm in the thickness of the Cu foil occurred after growth as shown in Fig. 1(d). The CuO NWs exhibited well resolved peaks in the XRD pattern as shown in Fig. 1(e) corresponding to the monoclinic crystal structure of CuO and also a few peaks due to the Cu<sub>2</sub>O.

A typical TEM image of the CuO NWs is illustrated in Fig. 2(a). They have a straight morphology with averaged projected diameters measured as  $d = 150 \pm 30$  nm. The corresponding selected area electron diffraction (SAED) pattern recorded along the [111] zone axis (z.a), shown in Fig. 2(b), confirms the base-centered monoclinic crystal structure of the CuO NWs. The 11 $\bar{2}$ , 11 $\bar{0}$  and 20 $\bar{2}$  reflections corresponding to the interplanar spacing ( $d$ -spacing) of the lattice planes are indicated. A HRTEM image from the surface of a CuO NW is presented in Fig. 2(c). A magnified image of the area bounded by the white frame is given as inset. The lattice fringe spacing, equal to 0.187 nm, corresponds to the  $d$ -spacing of the (20 $\bar{2}$ ) lattice planes of the CuO monoclinic structure.

For completeness it should be mentioned that the CuO NWs grow by a vapor–solid (VS) mechanism whereby Cu diffuses out of the underlying foil and oxygen diffuses inwards along grain boundaries, as illustrated in Fig. 1(f). An extensive description of the growth conditions and their optimization as well as



**Fig. 1** Growth of CuO NWs. (a) SEM image and (b) XRD pattern of the Cu foil that was used for the growth of the CuO NWs. (c) SEM image of the CuO NWs that grow on top of the Cu foil (d) Cross-section image of the Cu foil after removing the bulk CuO layer and CuO NWs (e) XRD pattern of the CuO NWs after being removed from the underlying Cu foil (f) schematic illustration of the growth of CuO NWs.



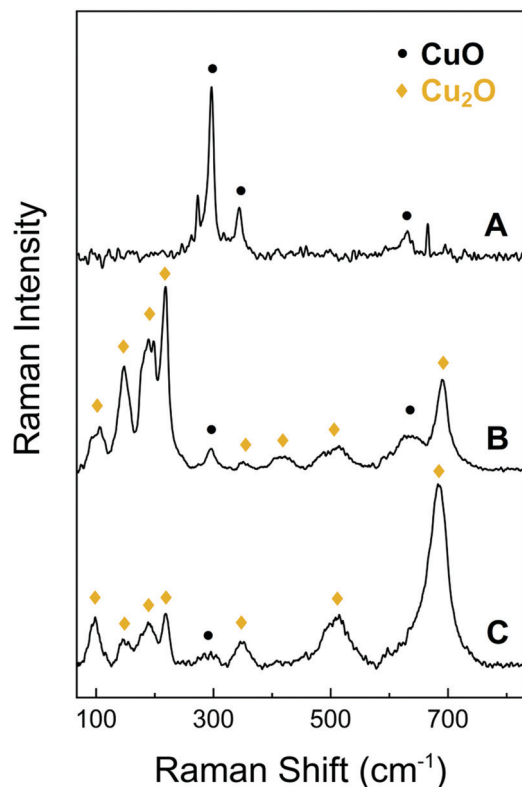


Fig. 2 Raman spectra of the CuO NWs (A), the bulk CuO layer that supports the CuO NWs after being detached from the underlying foil (B) and the surface of the bare Cu foil (C).

issues pertaining to the integrity of the CuO NW network is provided in the ESI,† S1.

In addition to the above, we investigated the structural properties of the CuO NWs by Raman spectroscopy and found that the conversion of the Cu to CuO NWs occurs gradually, from Cu to Cu<sub>2</sub>O and then to CuO. As expected, it is found that the CuO NWs consist only of CuO phase, as shown by trace A of Fig. 3. The Raman line observed at 290 cm<sup>-1</sup> can be attributed to the A<sub>g</sub> mode and the 345 and 630 cm<sup>-1</sup> peaks to the B<sub>g</sub> modes of the CuO phase.<sup>35</sup> The bulk layer supporting the CuO NWs contains both the CuO and Cu<sub>2</sub>O phases as indicated by trace B in Fig. 3. The peak observed at approximately 515 cm<sup>-1</sup>

can be assigned to the only Raman active mode T<sub>2g</sub> of Cu<sub>2</sub>O. The peaks at 110 cm<sup>-1</sup> (E<sub>u</sub>), 150 cm<sup>-1</sup> (T<sub>1u</sub>) and 350 cm<sup>-1</sup> (A<sub>2u</sub>) are observed as well and again these are attributed to the Cu<sub>2</sub>O phase. Additional features at 220 cm<sup>-1</sup> (2E<sub>u</sub>), in the vicinity of 400–450 cm<sup>-1</sup> and at 695 cm<sup>-1</sup> are due to multiphonon Raman scattering. Moreover, the signal observed at 190 cm<sup>-1</sup> is attributed to local vibrations of Cu on O-sites.<sup>36,37</sup> The surface of the Cu foil after the exfoliation of the CuO NWs had a dark red color due to the presence of the Cu<sub>2</sub>O phase as shown by trace C in Fig. 3; a minor contribution of CuO was also detected.

In short, a uniform distribution of crystalline CuO NWs over 15 × 30 mm Cu foils was obtained. The CuO NWs are straight, have diameters of 150 ± 30 nm, lengths of ~3–10 μm, a monoclinic crystal structure and do not contain any Cu<sub>2</sub>O or Cu.

### 3.2 Nitridation of CuO into Cu<sub>3</sub>N Nanowires

Initially we tried to reduce the CuO into Cu NWs under H<sub>2</sub> in order to subsequently convert them into Cu<sub>3</sub>N NWs under NH<sub>3</sub>:O<sub>2</sub> similar to the Cu<sub>3</sub>N layers that were obtained previously from Cu under NH<sub>3</sub>:O<sub>2</sub>.<sup>38</sup> We find that the CuO NWs can be reduced to Cu under H<sub>2</sub> at 300 °C but contain residual Cu<sub>2</sub>O and are shortened. The CuO NWs were eliminated above 400 °C, see ESI,† S2. We developed a strategy to preserve their integrity of the CuO NWs under reducing conditions *via* the deposition of a Cu shell over the CuO NWs in order to convert them into Cu<sub>3</sub>N under NH<sub>3</sub>:H<sub>2</sub>. More specifically Cu with a thickness of 240 nm was deposited on the CuO NWs and the CuO/Cu core-shell NWs were annealed at 400 °C for 60 min under 300:10 mL min<sup>-1</sup> NH<sub>3</sub>:H<sub>2</sub>, as illustrated in Fig. 4(a). The CuO/Cu core-shell NWs maintained their integrity and were converted into Cu<sub>3</sub>N NWs that acquired a curly shape as shown in Fig. 4(b) and exhibited well resolved peaks in the XRD pattern belonging to Cu<sub>3</sub>N as well as a single peak of low intensity at 2θ = 77.4° which may be indexed to the (222) crystallographic plane of the monoclinic crystal structure of Cu<sub>2</sub>O as shown in Fig. 4(c). The Cu<sub>3</sub>N phase was also identified by the major peaks of the optical modes T<sub>2u</sub> (170 cm<sup>-1</sup>) and T<sub>1u</sub> (655 cm<sup>-1</sup>),<sup>39</sup> in the Raman spectra shown in Fig. 4(d). A smaller contribution of the Cu<sub>2</sub>O phase, with peaks at *ca.* 150 and 220 cm<sup>-1</sup> is also detected. For comparison, the Raman spectrum recorded from a Cu<sub>3</sub>N thin film obtained from

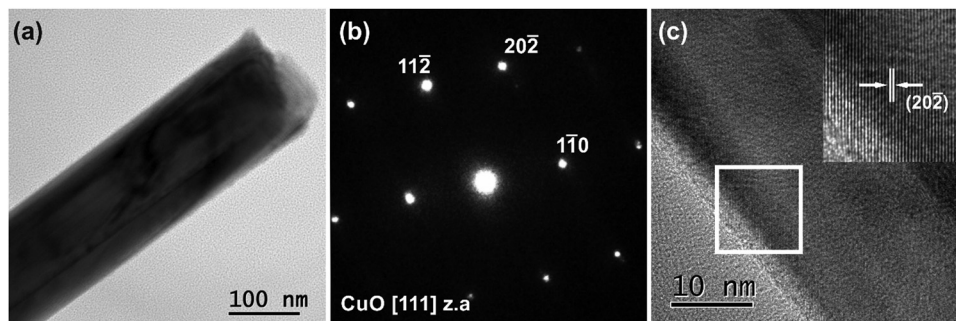


Fig. 3 (a) TEM image of a CuO NW along with (b) the corresponding SAED pattern recorded along the [111] zone axis of monoclinic CuO. (c) HRTEM image showing the edge side of a CuO NW and as inset, magnification of the area in the rectangle frame indicating the spacing of the (202) lattice fringes of CuO.



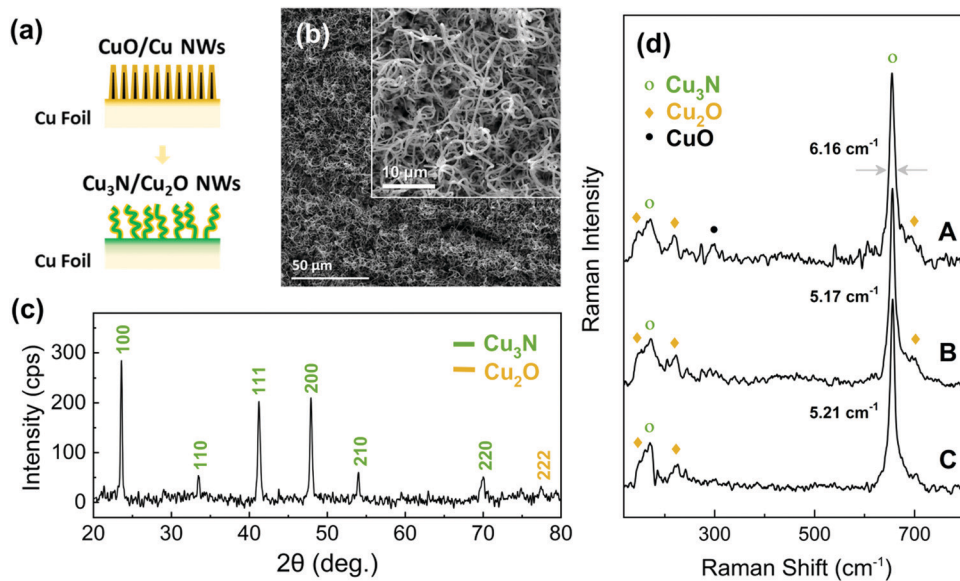


Fig. 4 (a) Schematic illustration of the conversion of the CuO into Cu<sub>3</sub>N NWs (b), (c) SEM image and XRD pattern of the Cu<sub>3</sub>N/Cu<sub>2</sub>O NWs obtained from the CuO NWs that were coated with 240 nm Cu (d) Raman spectra of the Cu<sub>3</sub>N/Cu<sub>2</sub>O NWs obtained from CuO NWs that were coated with 480 nm Cu (trace A) and 240 nm Cu (trace B) and treated under NH<sub>3</sub>: H<sub>2</sub>; also shown the case of a Cu<sub>3</sub>N thin film obtained from a 240 nm Cu layer that was deposited on a Cu foil and treated under NH<sub>3</sub>: H<sub>2</sub> (trace C).

annealing of a Cu foil under NH<sub>3</sub>:H<sub>2</sub> flow is shown at the bottom of Fig. 4(d). The Cu<sub>2</sub>O phase is also detected in this case and can be attributed to the surface native oxide of Cu<sub>3</sub>N. It is worth noting that the CuO NWs covered with a 480 nm Cu shell that were converted into Cu<sub>3</sub>N still contained CuO as shown in Fig. 4(d). This can be attributed to the incomplete conversion of the CuO NWs to Cu<sub>3</sub>N due to the fact that the oxygen atoms had to travel a longer distance in order to out-diffuse from the core during the nitridation process. Moreover, the peak at *ca.* 655 cm<sup>-1</sup> for the Cu<sub>3</sub>N NWs obtained from CuO NWs covered with a Cu shell of 480 nm is broader compared to that of the Cu<sub>3</sub>N NWs, obtained from CuO NWs covered with a thin shell of 240 nm, indicating a decrease in crystallinity.

In order to gain a deeper insight, the structural properties of the Cu<sub>3</sub>N NWs were investigated by TEM. A curly like morphology with rough side surfaces was observed, as shown in Fig. 5(a). The Cu<sub>3</sub>N NWs had a diameter  $d = 320 \pm 35$  nm. The strong

diffraction contrast of the image revealed that the Cu<sub>3</sub>N NWs actually consist of a CuO core with an averaged projected diameter of  $40 \pm 5$  nm. Detailed SAED analysis demonstrated that the Cu<sub>3</sub>N NWs are polycrystalline as confirmed by the ring SAED pattern shown in Fig. 5(b). The indexed rings, originating from misoriented crystallites, correspond to the interplanar spacing of 110, 111, 200, 210, 220 and 311 lattice planes of the cubic anti-ReO<sub>3</sub> structure of Cu<sub>3</sub>N. In the SAED pattern of Fig. 5(b) two additional rings were detected assigned to the interplanar spacing of 111 and 211 planes of the cubic Cu<sub>2</sub>O. The presence of Cu<sub>2</sub>O has been also confirmed by HRTEM observations. An HRTEM image recorded near the side surface of the Cu<sub>3</sub>N/Cu<sub>2</sub>O NW is presented in Fig. 5(c), while a magnification of the area in the rectangular frame (given as inset) illustrates its atomic structure, projected along the  $[\bar{1}10]$  z.a. of the cubic Cu<sub>2</sub>O. The viewing direction is also confirmed by the corresponding FFT (2nd inset), calculated from the HRTEM image, where the 111,

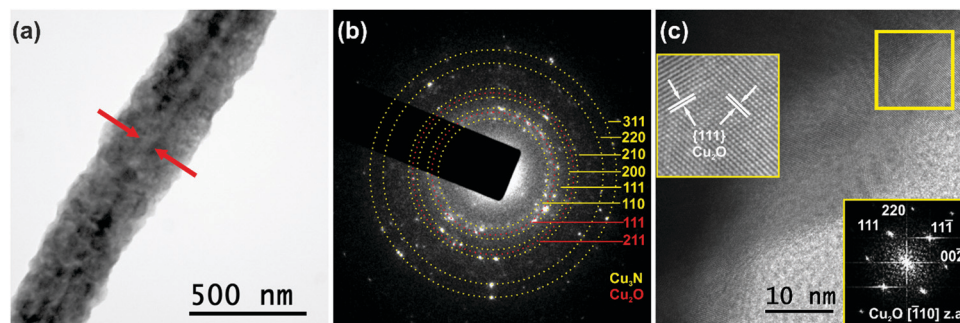


Fig. 5 (a) TEM image of a Cu<sub>2</sub>O/Cu<sub>3</sub>N core-shell NW; the CuO core is denoted by arrows. (b) Corresponding SAED pattern comprising diffraction rings that correspond to interplanar spacings of the cubic Cu<sub>2</sub>O and Cu<sub>3</sub>N structures. (c) HRTEM image of the side surface of a Cu<sub>3</sub>N/Cu<sub>2</sub>O NW; the two insets illustrate the atomic structure of the area in the rectangular frame viewed along the  $[\bar{1}10]$  Cu<sub>2</sub>O z.a. and the corresponding FFT.



$11\bar{1}$ ,  $00\bar{2}$ ,  $220$  spatial frequencies of the  $[\bar{1}10]$  z.a. are indicated. Two families of  $\{111\}$  lattice fringes of the cubic  $\text{Cu}_2\text{O}$  are indicated. It is estimated that a 30 nm  $\text{Cu}_2\text{O}$  oxide layer covers the surface of the  $\text{Cu}_3\text{N}$  NWs.

### 3.3 Ultrafast pump-probe spectroscopy of $\text{Cu}_3\text{N}/\text{Cu}_2\text{O}$ NWs

In order to measure the optical properties of the  $\text{Cu}_3\text{N}$  NWs by UPPS we removed  $\text{CuO}$  NWs from the  $\text{Cu}$  foil by sonication in isopropanol and dispersed them gradually on transparent fused silica ( $\text{f-SiO}_2$ ) after which they were converted into  $\text{Cu}_3\text{N}$  under  $\text{NH}_3:\text{H}_2$  at  $400^\circ\text{C}$  as shown in Fig. 6(a). The time evolution of the differential transmission ( $dT/T$ ) on a ps time scale is shown in Fig. 6(b and c) for different probe wavelengths  $\lambda_{\text{PR}}$  that vary between 450 and 750 nm after ‘pumping’ the  $\text{Cu}_3\text{N}$  NWs with light having a wavelength of  $\lambda_{\text{PU}} = 260$  nm and incident energy of 1 and  $5\ \mu\text{J}$  respectively. The incident energy was varied between 1 and  $5\ \mu\text{J}$  to avoid the generation of an overtly high carrier density which leads to a smearing of the spectral structure as we have shown previously.<sup>38</sup> In essence the photoexcited electrons will occupy states in the conduction band and recombine over a few tens of ps by moving to states with lower energy, during which the transmission of light with wavelengths that vary between 450 and 750 nm is measured, to find out which states are occupied thereby revealing their energetic position and giving insight into the actual electronic band structure. The  $\text{Cu}_3\text{N}$  NWs exhibited maxima at 515 nm ( $\equiv 2.41$  eV), 570 nm ( $\equiv 2.17$  eV), 650 nm ( $\equiv 1.91$  eV) and

690 nm ( $\equiv 1.8$  eV) as measured by UPPS that are shown in Fig. 6(b and c). The lower energy duo of maxima at  $\lambda_{\text{PR}} = 650$  nm ( $\equiv 1.91$  eV) and 690 nm ( $\equiv 1.8$  eV) correspond to the M and R direct energy band gaps of bulk- $\text{Cu}_3\text{N}$  in good agreement with the electronic structure depicted in Fig. 7(a) while the higher energy maxima at 515 nm ( $\equiv 2.41$  eV) and 570 nm ( $\equiv 2.17$  eV) correspond to the  $M^*$  and  $R^*$  direct gaps of  $\text{Cu}_3\text{N}$  under tensile strain that arise due to the formation of  $\text{Cu}_2\text{O}$  on  $\text{Cu}_3\text{N}$  as shown in Fig. 7(b). The spectral structure shown in Fig. 6(b and c) is very similar to that obtained from  $\text{Cu}_3\text{N}$  layers obtained previously from  $\text{Cu}$  under a flow of  $\text{NH}_3:\text{O}_2$  between 400 and  $600^\circ\text{C}$ .<sup>38</sup> The  $\text{Cu}_3\text{N}$  layers obtained previously exhibited distinct maxima in differential transmission ( $dT/T$ ) on a ps time scale at 500 nm ( $\equiv 2.48$  eV), 550 nm ( $\equiv 2.25$  eV), 630 nm ( $\equiv 1.97$  eV) and 670 nm ( $\equiv 1.85$  eV). We showed that the maxima at 1.97 eV and 1.85 eV correspond to the M and R direct energy band gaps of bulk  $\text{Cu}_3\text{N}$  in excellent agreement with density functional theory (DFT) calculations of the electronic band structure. This observation of the M and R direct energy band gaps of  $\text{Cu}_3\text{N}$  was possible by virtue of the fact that crystal imperfections, such as N vacancies ( $V_{\text{N}}$ ), Cu interstitials ( $\text{Cu}_i$ ) etc. give rise to states that are energetically located very close or inside the conduction and valence band edges as shown by Yee *et al.* who investigated the properties of N-rich  $\text{Cu}_3\text{N}$  and confirmed the existence of Cu interstitials ( $\text{Cu}_i$ ) by photo thermal deflection spectroscopy (PDS). The latter is an indirect method with dramatically higher sensitivity than steady state

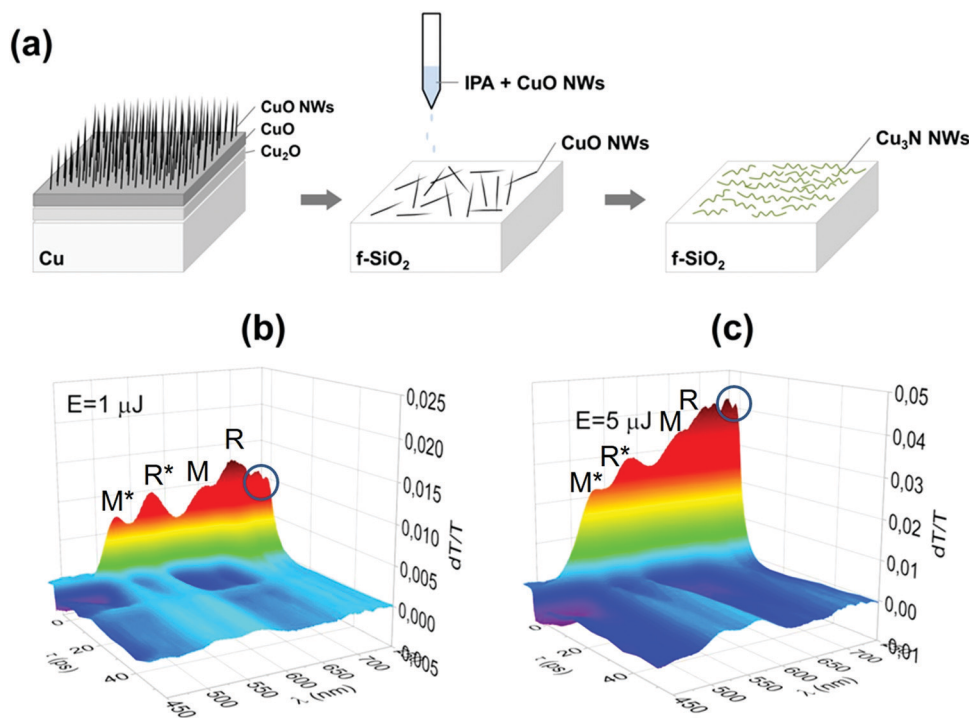


Fig. 6 (a) Schematic illustration of the isolation and conversion of  $\text{CuO}$  into  $\text{Cu}_3\text{N}/\text{Cu}_2\text{O}$  NWs. UPPS of  $\text{Cu}_3\text{N}/\text{Cu}_2\text{O}$  NWs on  $\text{f-SiO}_2$  showing the differential transmission  $dT/T$  on the vertical axis (no units) versus time delay  $\tau$  (ps) and probe wavelength  $\lambda$  (nm) for incident energies of (b)  $E = 1\ \mu\text{J}$  and (c)  $E = 5\ \mu\text{J}$ . The maxima at 515 nm ( $\equiv 2.41$  eV), 570 nm ( $\equiv 2.17$  eV) correspond to the  $M^*$  and  $R^*$  direct band gaps of  $\text{Cu}_3\text{N}$  under tensile strain while those at 650 nm ( $\equiv 1.91$  eV) and 690 nm ( $\equiv 1.8$  eV) correspond to the M and R bulk band gaps of  $\text{Cu}_3\text{N}$ . The encircled, minor peaks at 730 nm ( $\equiv 1.69$  eV) and 740 nm ( $\equiv 1.67$  eV) may be attributed to states in  $\text{Cu}_2\text{O}$  or to the  $M^*$  and  $R^*$  direct band gaps of  $\text{Cu}_3\text{N}$  under compressive strain.



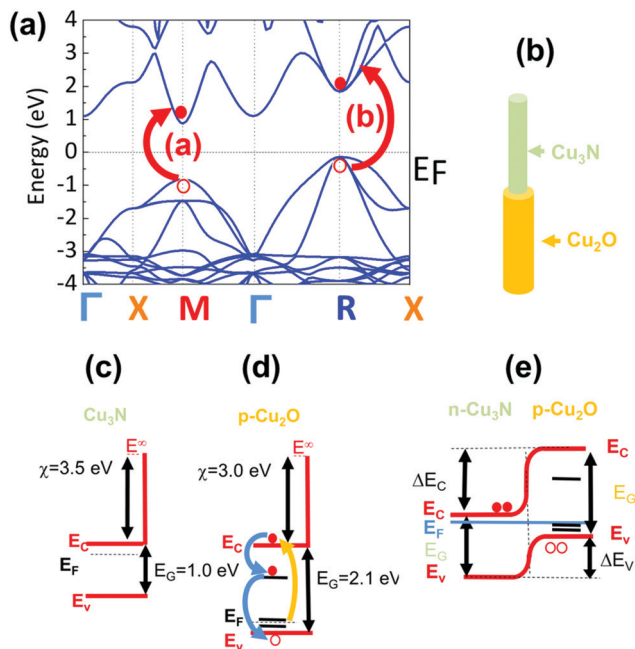


Fig. 7 (a) Electronic structure of  $\text{Cu}_3\text{N}$  showing the excitation of an electron and its transition across the M and R direct energy bandgaps in good agreement with the energetic position of the maxima in differential transmission observed at 1.91 eV and 1.8 eV corresponding to bulk  $\text{Cu}_3\text{N}$  (b) schematic of a  $\text{Cu}_3\text{N}/\text{Cu}_2\text{O}$  core-shell NW (c), (d) energy band diagrams of  $\text{Cu}_3\text{N}$  and  $\text{Cu}_2\text{O}$  showing the states at  $\sim 0.16$  eV above  $E_V$  and  $\sim 0.4$  eV below  $E_C$  (e) energy band diagram of a p-n heterojunction  $\text{Cu}_3\text{N}/\text{Cu}_2\text{O}$  core-shell NW.

UV-vis spectroscopy that can be used for the detection of sub-band-gap states that are related to crystal imperfections and/or impurities. In addition, we showed that the maxima at 2.48 eV and 2.25 eV correspond to the M and R direct gaps of certain regions of  $\text{Cu}_3\text{N}$  layers under tensile strain that arise due to the formation of  $\text{CuO}$  and  $\text{Cu}_2\text{O}$ , *via* the out-diffusion of oxygen from the underlying fused silica ( $\text{f-SiO}_2$ ) and/or surface oxidation.<sup>40</sup> The spectral structure of the  $\text{Cu}_3\text{N}/\text{Cu}_2\text{O}$  NWs shown in Fig. 6(b and c) is similar to that obtained previously from  $\text{Cu}_3\text{N}$  layers<sup>38</sup> but we do not observe any quantization effects, as the peaks corresponding to bulk  $\text{Cu}_3\text{N}$  are not blue-shifted to higher energies. However the  $\text{Cu}_3\text{N}$  NWs exhibited peaks at 730 nm ( $\equiv 1.69$  eV) and 740 nm ( $\equiv 1.67$  eV) shown in Fig. 6(b and c) that were not observed in our previous investigations of  $\text{Cu}_3\text{N}$  layers. The maxima at 730 nm ( $\equiv 1.69$  eV) and 740 nm ( $\equiv 1.67$  eV) may correspond to the  $M^*$  and  $R^*$  direct gaps of the  $\text{Cu}_3\text{N}$  closer to the core that could be under compressive strain. These values are close to those found by Birket *et al.*<sup>8</sup> who investigated the variation of the energy band-gap with temperature using Fourier transform infra-red spectroscopy. They prepared  $\text{Cu}_3\text{N}$  by sputtering under Ar and  $\text{N}_2$  and the direct energy band gap was found to be 1.68 eV at 300 K but changed only very slightly up to 1.7 eV at 4.2 K. However, Birket *et al.*<sup>8</sup> showed that the direct and indirect band gap changes from 1.4 eV to 2.0 eV and 0.6 eV to 1.8 eV respectively upon increasing the lattice constant from 3.8 Å to 3.9 Å. Consequently, structural distortion has a pronounced

effect on the values of the direct and indirect band-gap and by extension on the optical band gap. This is most likely why there is such a broad variation in the optical band gaps of  $\text{Cu}_3\text{N}$  determined previously by others using steady state optical spectroscopy, *i.e.* UV-vis absorption-transmission, reflectance-transmission spectroscopy, ellipsometry that vary between 1.2 to 2.4 eV.<sup>41–51</sup> Alternatively, the maxima observed at 730 nm ( $\equiv 1.69$  eV) and 740 nm ( $\equiv 1.67$  eV) in Fig. 6(b and c) may be related to transitions between states in the  $\text{Cu}_2\text{O}$  shell. It is useful to mention at this point that  $\text{Cu}_2\text{O}$  is a p-type metal-oxide semiconductor that has a direct energy band-gap of 2.1 eV and the Fermi level at the surface is pinned at surface states residing  $\sim 0.4$  eV below the conduction band edge leading to a depletion.<sup>52</sup> It should also be pointed out that  $\text{Cu}_2\text{O}$  has acceptor like states located  $\sim 0.16$  eV above the valence band maximum that are related to copper vacancies ( $V_{\text{Cu}}$ ) and give rise to its native p-type conductivity.<sup>40,53</sup> Consequently the maxima observed at 730 nm ( $\equiv 1.69$  eV) and 740 nm ( $\equiv 1.67$  eV) in Fig. 6(b and c) may be related to transitions between these states that are shown schematically in Fig. 7(d).

The energy band diagram of the  $\text{Cu}_3\text{N}/\text{Cu}_2\text{O}$  core-shell NW is shown in Fig. 7(e). We have shown previously that oxygen on nitrogen sites ( $O_{\text{N}}$ ) have the lowest formation energy and oxygen acts as a donor in  $\text{Cu}_3\text{N}$ .<sup>40</sup> Consequently, the  $\text{Cu}_3\text{N}$  is expected to be n-type in contrast to  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  that are p-type, hence the  $\text{Cu}_3\text{N}/\text{Cu}_2\text{O}$  core-shell NW is a p-n heterojunction. It should be mentioned that  $\text{Cu}_2\text{O}$  which is the native oxide of  $\text{Cu}_3\text{N}$  was suggested<sup>3</sup> that could act in a beneficial way to  $\text{Cu}_3\text{N}$  as a surface passivation layer similar to  $\text{SiO}_2$  in Si solar cells. However, the lifetime of the photogenerated electron-hole pairs is of the order of a few tens of ps as shown by the time evolution of the differential transmission in Fig. 6(b and c) which implies that the photoexcited carriers quickly recombine so the idea that  $\text{Cu}_2\text{O}$  may act as a passivation layer for  $\text{Cu}_3\text{N}$  may not be so valid in reality. Finally it should be pointed out that despite the fact that  $\text{Cu}_3\text{N}$  has a “clean bandgap” with no mid gap states and has been described to be a defect tolerant semiconductor that is attractive as a solar cell absorber, no one has so far fabricated a p-n junction solar cell using  $\text{Cu}_3\text{N}$  that exhibits photovoltaic action. In the past, Chen *et al.*<sup>54</sup> fabricated a p-n  $\text{Cu}_3\text{N}$  homo junction on indium tin oxide (ITO) and Yee *et al.*<sup>55</sup> fabricated an Al:  $\text{ZnO}/\text{ZnS}/\text{Cu}_3\text{N}$  p-n heterojunction both of which showed rectifying behavior, but no photo generated current, attributed to a high density of N vacancies ( $V_{\text{N}}$ ) and Cu interstitials ( $\text{Cu}_i$ ) that capture electrons and result into significant Shockley-Read-Hall recombination and suppression of the photogenerated electron-hole pairs. So, while crystal defects such as  $V_{\text{N}}$  and  $\text{Cu}_i$ , do not give rise to mid-gap states they still act in a detrimental fashion that hinders the use of  $\text{Cu}_3\text{N}$  as a defect tolerant semiconductor for the fabrication of solar cells. One way of overcoming these difficulties is to grow  $\text{Cu}_3\text{N}$  nanostructures on epitaxial, high crystal quality, transparent conducting oxides *e.g.* Sb:  $\text{SnO}_2$  NWs which will permit the extraction of the minority carriers over shorter lengths so that  $\text{Cu}_3\text{N}$  may be used for energy conversion as a solar cell absorber. Nevertheless, the  $\text{Cu}_3\text{N}$  NWs obtained here



that have diameters between 100 and 200 nm and lengths up to  $\sim 10 \mu\text{m}$  can be used directly for energy storage as they have a large surface area and can be easily removed and transferred onto a flexible substrate for the purpose of making devices such as supercapacitors or batteries.

## 4. Conclusions

CuO NWs with diameters of  $150 \pm 30 \text{ nm}$ , lengths up to  $3\text{--}10 \mu\text{m}$  and a uniform distribution have been grown *via* the thermal oxidation of Cu foils at  $600^\circ\text{C}$  under  $\text{O}_2$ . The CuO NWs have a monoclinic crystal structure and grow by a vapor–solid mechanism on top of bulk CuO and  $\text{Cu}_2\text{O}$  that forms first on top of the Cu foil. We developed a strategy to convert the CuO into  $\text{Cu}_3\text{N}$  NWs under  $\text{NH}_3\text{:H}_2$  *via* the deposition of Cu over the CuO NWs in order to maintain their integrity under reducing conditions. The  $\text{Cu}_3\text{N}$  NWs obtained in this way are curly, have a cubic anti- $\text{ReO}_3$  crystal structure but are surrounded by a surface shell of  $\text{Cu}_2\text{O}$ . The CuO NWs with a 480 nm shell of Cu are not converted completely into  $\text{Cu}_3\text{N}$  and consist of a CuO core with thicknesses of a few tens of nm *i.e.* the CuO/ $\text{Cu}_3\text{N}$  core–shell NWs have an averaged projected diameter  $d = 320 \pm 35 \text{ nm}$ ;  $40 \pm 5 \text{ nm}$  for the core.

The  $\text{Cu}_3\text{N}$  NWs exhibited maxima in differential transmission at 2.41, 2.17, 1.9 and 1.8 eV as measured by UPPS that correspond to the M and R direct energy band gaps of  $\text{Cu}_3\text{N}$  but we find no evidence for quantization. In addition, we observed two minor, but well resolved peaks close to the infra-red at 1.69 and 1.67 eV that may be attributed to the M and R direct energy band gaps of  $\text{Cu}_3\text{N}$  under compression or due to recombination *via* states in the  $\text{Cu}_2\text{O}$ . The photogenerated carriers have lifetimes less than 100 ps, so the potential of  $\text{Cu}_3\text{N}$  as a defect tolerant semiconductor-solar cell absorber for energy conversion is currently limited in contrast to that for energy storage.

## Conflicts of interest

The author declares no competing interest.

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