Electronic Supplementary Material (ESI) for CrystEngComm
This journal is © The Royal Society of Chemistry 2012

Electronic Supplementary Information

# Large-scale synthesis of Cu nanowires with gradient scales by using "hard" strategies and size effects on electrical properties

Yuxin Zhao,[a, b] Zezhong Zhang,[a] Ying Zhang*[a], Yanpeng Li,[a] Zhaoyang He[c] and Zifeng Yan*[a]

[a]State Key Laboratory for Heavy Oil Processing, Key Laboratory of Catalysis, CNPC, China University of Petroleum, Qingdao 266555, China.

[b] QLD Micro-and Nanotechnology Centre, Nathan Campus, Griffith University, QLD 4111, Australia.

[c] Oil and Gas Control Center of PetroChina, Dongcheng District, Beijing 100007, China.

The strategies for growing such highly anisotropic solid nanostructures usually involve nucleation and growth stages for crystallization of a solid from a vapor, a liquid, or a solid phase. Generally, the synthesis strategies of Cu NWs based on the basic nucleation and crystal growth theories can be classified into two types: the "soft" approaches and the "hard" approaches, according to their reaction conditions.

**Soft syntheses**

Among the "soft" approaches, drastic reaction conditions (high temperature, high pressure, etc.) are not needed, these routes are usually based on solution chemistry which are initiated under mild conditions or under natural conditions. Presently, there is a challenge to turn down the heat for the crystal growth and find lower energy consumption, inexpensive, simple crafts and environmentally friendly pathway for the fabrication as far as possible.

**Hard syntheses**

Among the "hard" approaches, the templates are usually foreign hard and reaction conditions are drastic, for instance, the reaction media was commonly a gas phase while the high vacuum system and high temperature are needed according to these approaches. The defects of these methods are complex reaction process, high cost and energy consumption, which will be the bottleneck of their development. The generic hard methods suitable for all solid materials include the following types:

This journal is © The Royal Society of Chemistry 2012

1. Vapor-solid (VS) synthesis, in principle, the NWs are generated from vapor condensation onto a substrate. In this mechanism, the driving force for 1D growth was determined by an axial screw dislocation, and incoming atoms could adsorb onto the entire surface of a nanowire and then migrate towards the growing tip.

2. Vapor-Liquid-Solid (VLS) synthesis, a typical VLS process starts with the dissolution of gaseous reactants into nanosized liquid droplets of a catalyst metal, followed by nucleation and growth of single-crystalline rods and then wires.

3. Template-directed synthesis, in which the hard templates such as carbon nanotubes (CNTs), porous silica and porous aluminum templates are used.

The main existing hard synthesis methods for fabricate Cu NWs are limited to VS approaches (such as CVD and MOCVD routes) and template-directed approaches, meanwhile, these two processes are not isolated, they exist relations and influence each other and usually can be combined to achieve better results.

**Table S1** The conditions and structural variation of each synthetic methods

| **Hard approaches** | | | |
|---|---|---|---|
| **Name** | **Conditions** | **Morphology of NWs** | **Composition & structural characteristic** |
| Template-assisted MOCVD | With template assisted<br>Pressure: 0.01 bar;<br>$N_2/H_2$ (95:5) mixed carrier gas;<br>Temperature: 400°C;<br>Duration time: 40 min. | Diameter: 7-10 nm, length: over 3 μm;<br>unidentifiable geometrical shapes at tail end as a result of the line edge roughness which is induced by the etching process. | Pure copper<br>(single crystal) |
| Template-free MOCVD | Pressure: 0.01 bar;<br>$Ar/O_2$ ($VO_2$ %=12%) mixed carrier gas;<br>Temperature: 450°C;<br>Duration time: 45 min. | Diameter: 35-120 nm, length: over 10 μm;<br>the edge shape of 45% Cu NWs are pentagonal pyramid and the others are approximate cylindrical due to the pre-melting. | Pure copper<br>(single crystal) |
| | $Ar/O_2$ ($VO_2$ %<12%) mixed carrier gas;<br>other things being equal | | Copper@carbon<br>(graphite) |
| | $Ar/O_2$ ($VO_2$ %>12%) mixed carrier gas;<br>other things being equal | | CuO and $Cu_2O$ |
| Redox thermal process of C/Cu grid | Pressure: 0.1 bar;<br>$Ar/O_2$ ($VO_2$ %=7%) mixed carrier gas;<br>Temperature: 350°C;<br>Duration time: 3 h. | Diameter: 120-200 nm, length: 10-20 μm;<br>unidentifiable geometrical shapes at tail end as a result of breakage during fabrication and collection process. | Pure copper<br>(single crystal) |
| | Temperature: <350°C;<br>other things being equal | | Copper@carbon<br>(amorphous) |
| | Temperature: >350°C;<br>other things being equal | | Twisted copper rods and irregular particles<br>(single crystal in some small parts of region) |

This journal is © The Royal Society of Chemistry 2012

**Electrical measurement.** Our experiments were performed in a UHV-SEM system equipped with a CAPRES A/S M4PP monolithic Microscopic Four-Point Probes serving as a manipulator. The probes consist of four sharpened silicon oxide cantilevers, in line and equidistant from each other, extending from a silicon support chip. The silicon oxide paths on the chip are undercut, so that deposition of metal (Ti/Au alloy) onto the chip results in conducting paths that are insulated from the support chip. The probe chip is mounted on a ceramic plate which is set on a probe holder that has electrical contacts from the extern alcircuit to the probe. The probe holder is introduced with a manipulating arm into a main UHV chamber of SEM. This technique enables direct measurements of surface electrical conductivity at temperature induced surface phase transitions as well as detailed analysis of the carrier scattering mechanism at the surface layers of crystals. Moreover, the conductivity measurements can be done not only at room temperature, which expands the physics we can discuss from the data. Nanowires was placed on top of the contacts to avoid mechanical deformation of the wires, resistances of the order of gigaohms were recorded.

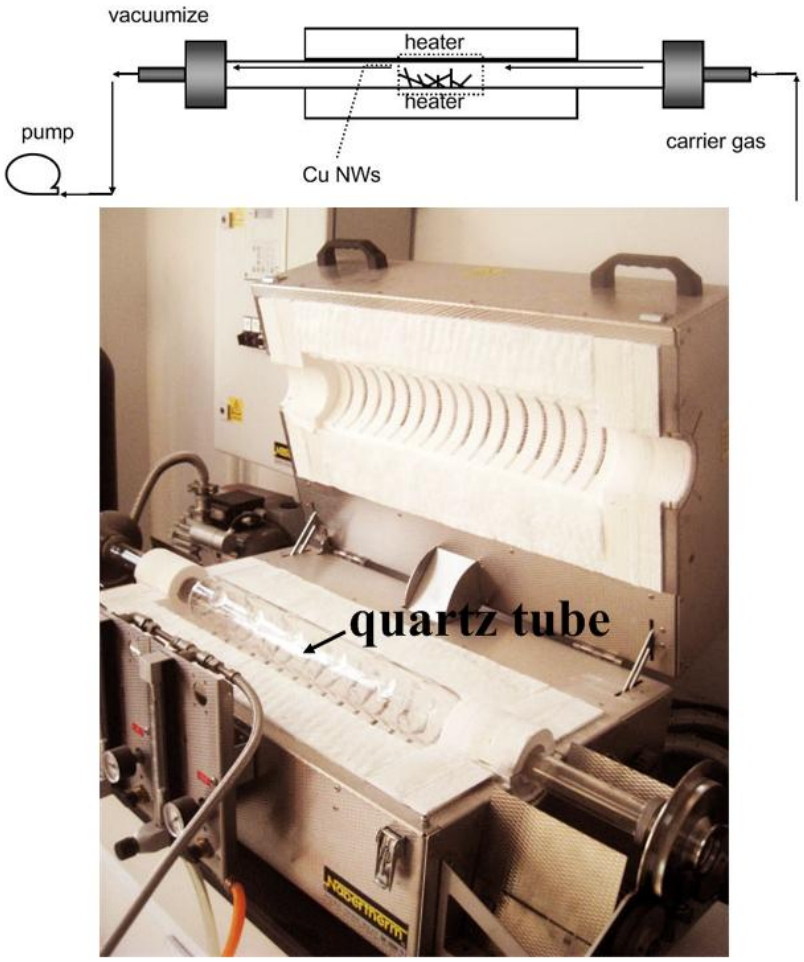


**Figure S1.** Schematic image of the "hard" preparation apparatus.

This journal is © The Royal Society of Chemistry 2012

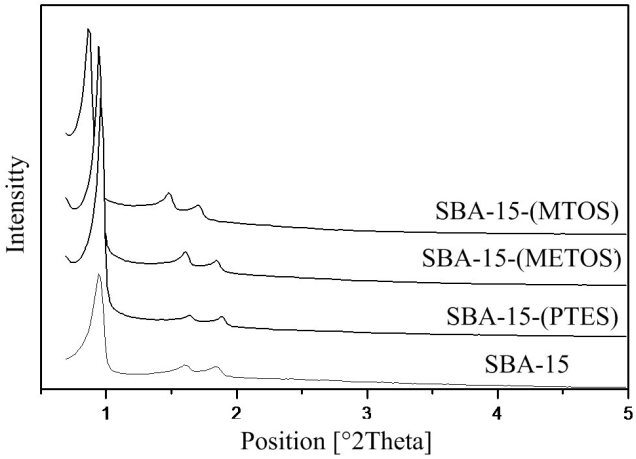


**Figure S2.** Small-angle XRD spectra of SBA-15 modified by different modifying agent.

**Table S2 $N_2$ adsorption data of different SBA-1**

| Sample | $S_{BET}(m^2/g)$ | $V_t(cm^3/g)$ | $D_{ave}(nm)$ |
|---|---|---|---|
| SBA-15 | 981.6 | 1.11 | 5.65 |
| SBA-15-MTOS | 582.2 | 1.12 | 7.57 |
| SBA-15-METOS | 529.6 | 1.13 | 6.38 |
| SBA-15-PTES | 843.4 | 1.05 | 5.29 |

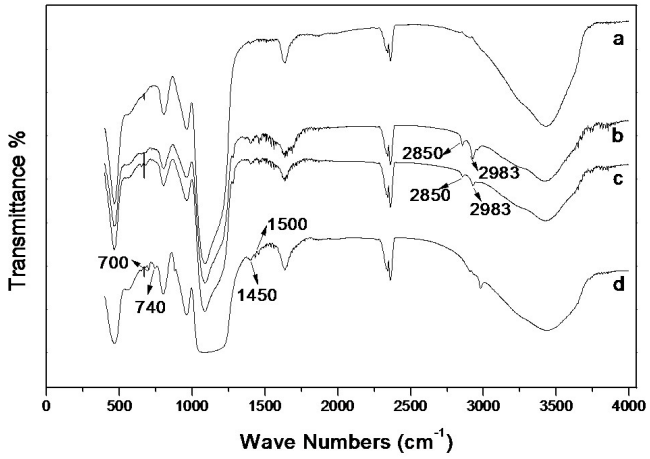


**Figure S3.** FT-IR spectra of different SBA-15: a) SBA-15; b) SBA-15-MTOS; c) SBA-15-METOS; d) SBA-15-PTES.

**Table S3 $N_2$ adsorption data of SBA-15-PTES and SBA-15-PTES-Cu.**

| Sample | $S_{BET}(m^2/g)$ | $V_t(cm^3/g)$ | $D_{ave}(nm)$ |
|---|---|---|---|
| SBA-15-PTES | 843.4 | 1.05 | 5.29 |
| SBA-15-PTES-Cu | 412.4 | 0.60 | 4.66 |

This journal is © The Royal Society of Chemistry 2012

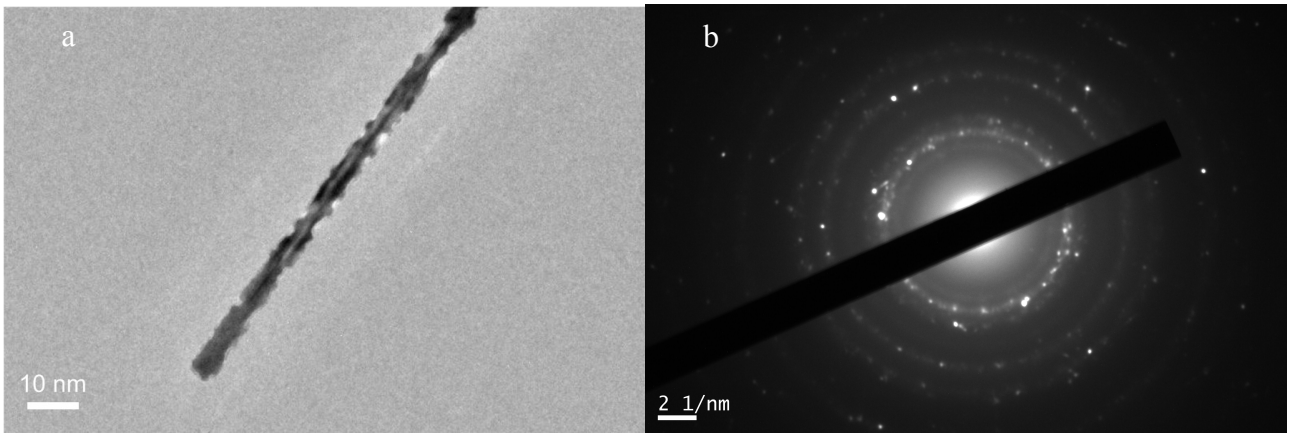


**Figure S4.** (a) TEM image of a single Cu NW (prepared by SCFD route) after removing silica frame of SBA-15 and (b) is an corresponding SAED pattern.

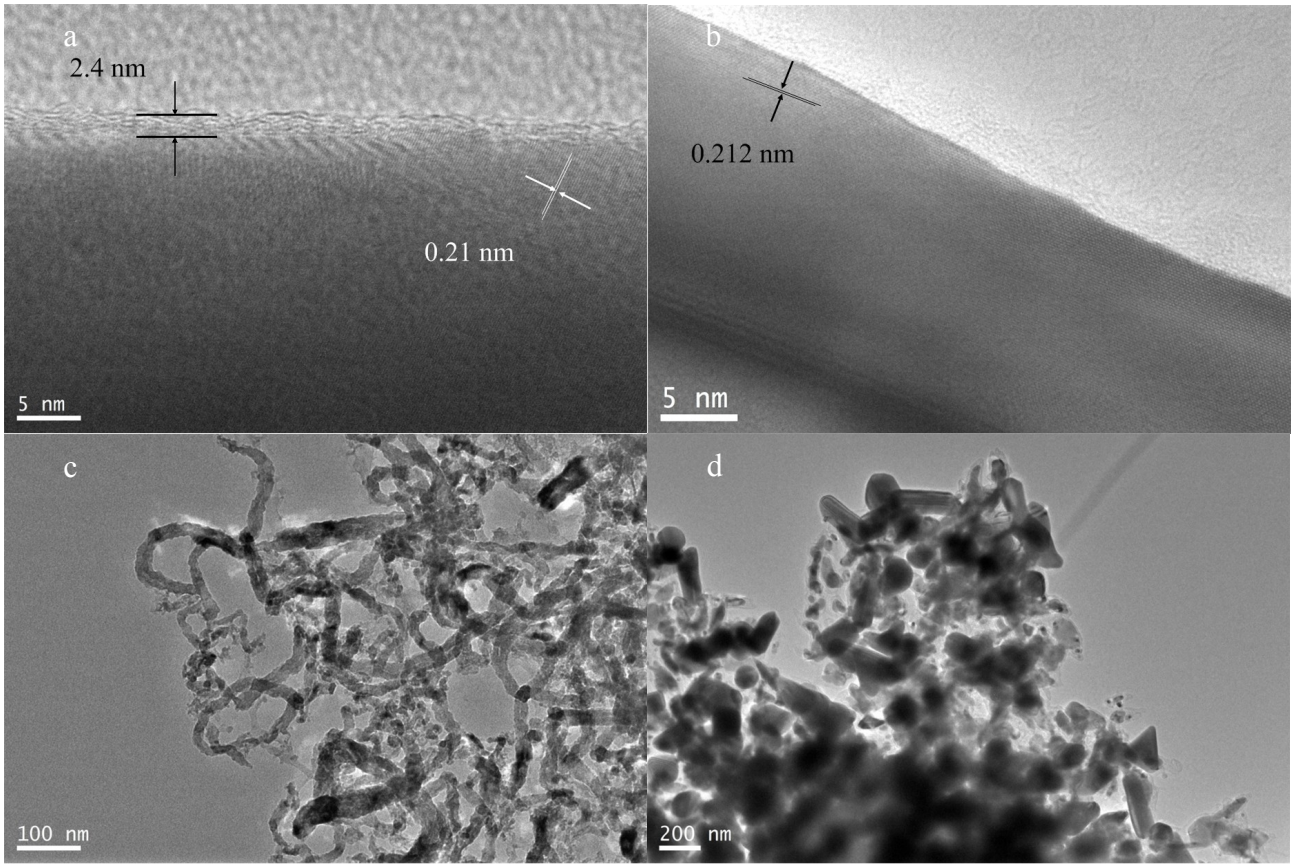


**Figure S5.** TEM/HRTEM analysis of interior structural characteristics of as-obtained products prepared at different temperature by fixing the other reaction conditions (duration time 3 h, pressure 0.1 bar, etc): (a) 290° C; (b) 350° C; (c) 400° C; (d) 450° C.

This journal is © The Royal Society of Chemistry 2012

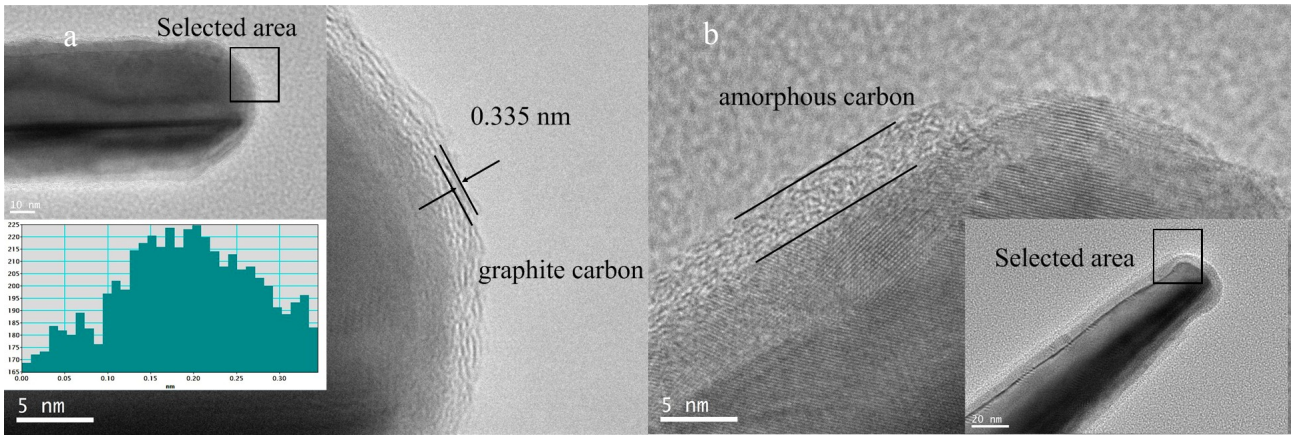


**Figure S6.** HRTEM images of as-prepared sample by using template-free MOCVD approach with 0% oxygen content flow gas for 1 h at different temperature: (a) 450° C, (b) 500 ° C, which clearly demonstrates 1-4 nm layers surrounding the Cu NW core synthesized at relatively low temperature are indeed well-crystallized graphene sheaths, in contrast, Cu NWs fabricated at high temperature covered with an amorphous carbon layer with a thickness of 4-7 nm.

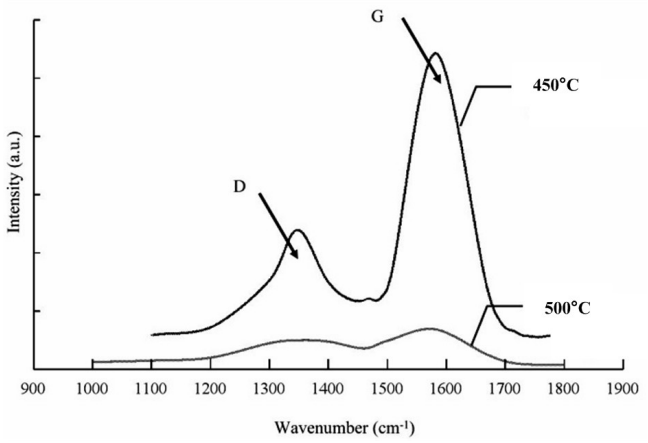


**Fig. S7.** Raman spectra of carbon shells grown on Cu NWs by template-free MOCVD method at different temperature. The intensity ratio of D-band to G-band ($I_D/I_G$) indicates the extent of defects within carbon shells, and smaller the value of $I_D/I_G$ is, the lesser the structural defects in shells would be. The result shows that $I_D/I_G$ decreases when change synthesis temperature which agree well with the HRTEM observations.

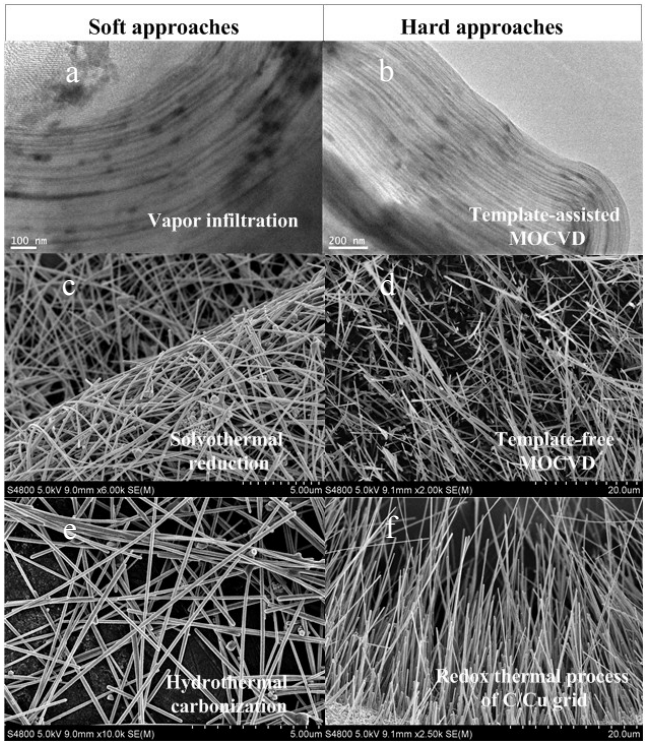


**Figure S8.** Cu NW products with different morphology of various syntheses investigated by TEM/SEM. (a) Vapor infiltration method; (b) template-assisted MOCVD method; (c) solvethermal reaction method; (d) template-free MOCVD method; (e) hydrothermal carbonization method and (f) redox process via thermal treatment of C/Cu grid method.