Nanotubular self-assembly of *n*-dodecylamine/TEOS/water/acetonitrile mixtures

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Electronic supporting information (ESI)

Materials preparation

In a typical synthesis of nanotubes (NT), 0.6 mmol *n*-dodecylamine (0.14 mL), 2 mmol tetraethoxyorthosilicate (TEOS, 0.45 mL), 0.2 g metal salt (i.e. $FeCl_2$, $RuCl_3$, $CuCl_2$, $NiCl_2$), 2 mL water and 2 mL acetonitrile were added to a microwave tube and microwaved for 1 to 15 min at 200W (maximum temperature reached 80-110^oC depending on the material). Materials were denoted as metal-Microwave Induced NanoTubes (metal-MINT; e.g. Cu-MINT). Alternatively, the preparation of NT was carried out under conventional heating (70^oC), under identical conditions to those reported in the microwave protocol, to compare results. These materials were simply denoted as metal-NanoTubes (e.g. Fe-NT). The resultant coloured solid was filtered off, thoroughly washed with acetonitrile and acetone and dried overnight at 100^oC before extracting the template in refluxing ethanol (5 h). Materials were then oven dried (100^oC) overnight and further characterised.

Characterisation

Materials were characterised by means of several techniques including Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Nitrogen physisorption and X-Ray Photoelectron Spectroscopy (XPS).

SEM micrographs were recorded in a JEOL JSM-6490LV. Samples were Au/Pd coated on a high resolution sputter SC7640 at a sputtering rate of 1500V per minute, up to 7 nm thickness.

TEM micrographs were recorded on a FEI Tecnai G^2 fitted with a CCD camera for ease and speed of use. The resolution is around 0.4 nm. Samples were suspended in ethanol and deposited straight away on a copper grid prior to analysis.

Nitrogen adsorption measurements were carried out at 77 K using an ASAP 2010 volumetric adsorption analyzer from Micromeritics. The samples were outgassed for 2 h at 100^oC under vacuum ($p< 10^{-2}$ Pa) and subsequently analyzed. The linear part of the

BET equation (relative pressure between 0.05 and 0.22) was used for the determination of the specific surface area. Materials were found to be mostly microporous.

XPS (aka ESCA) measurements were performed in a ultra high vacuum (UHV) multipurpose surface analysis system (Specs^{TM} model, Germany) operating at pressures $<10^{-10}$ mbar using a conventional X-Ray source (XR-50, Specs, Mg-Kα, 1253.6 eV) in a "stop-and-go" mode to reduce potential damage due to sample irradiation. The survey and detailed Fe and Cu high-resolution spectra (pass energy 25 and 10 eV, step size 1 and 0.1 eV, respectively) were recorded at room temperature with a Phoibos 150-MCD energy analyser. Powdered samples were deposited on a sample holder using double-sided adhesive tape and subsequently evacuated under vacuum ($<10^{-6}$ Torr) overnight. Eventually, the sample holder containing the degassed sample was transferred to the analysis chamber for XPS studies. Binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon.[1] The curve deconvolution of the obtained XPS spectra were obtained using the Casa XPS program.

The metal content in the materials was determined using Inductively Coupled Plasma (ICP) in a Philips PU 70000 secuential spectrometer equipped with an Echelle monochromator (0.0075 nm resolution). Samples were digested in HNO_3 and subsequently analysed by ICP at the University of Newcastle.

RESULTS AND DISCUSSION

Table 1. Textural properties including Surface area (S_{BET}, $m^2\ g^{-1}$), pore diameter (D_{BJH}, nm) and pore volume (V_{BJH}, mL g^{-1}) and metal loading as determined by elemental analysis of Fe and Cu materials.

Material	Surface area (S_{BET}, $m^2\ g^{-1}$)	Pore diameter (D_{BJH}, nm)	Pore volume (V_{BJH}, mL g^{-1})	Metal loading (wt%)
Fe-MINT	97	-[a]	0.38	0.49
Fe-NT	181	-	0.21	0.54
Cu-MINT	586	-	0.25	0.51
copper-NT	192	-	0.20	0.55

[a]Microporous

Cu-MWNT materials were observed to have an unexpectedly higher surface area compared to other Cu and Fe materials (Table 1) and this is related to the inherent bigger microporosity present in this material compared to the others. This remarkable difference in microporosity can be observed only for the Cu-microwave material and has been clearly demonstrated in the nitrogen adsorption/desorption curve included in Figure 1S bottom. This isotherm is completely different to those obtained for Fe-MINT and Cu and Fe-NT, showing a remarkably superior microporosity that is likely to be the case for the increase of the surface area, in a similar way to the increase in microporosity and surface area for Fe-NT (181 m^2 g^{-1}) compared to Fe-MINT (97 m^2 g^{-1}) . It is well-known that an increase in the microporosity of the materials considerably increases their surface areas (e.g. microporous carbons, zeolites and so on) [2].

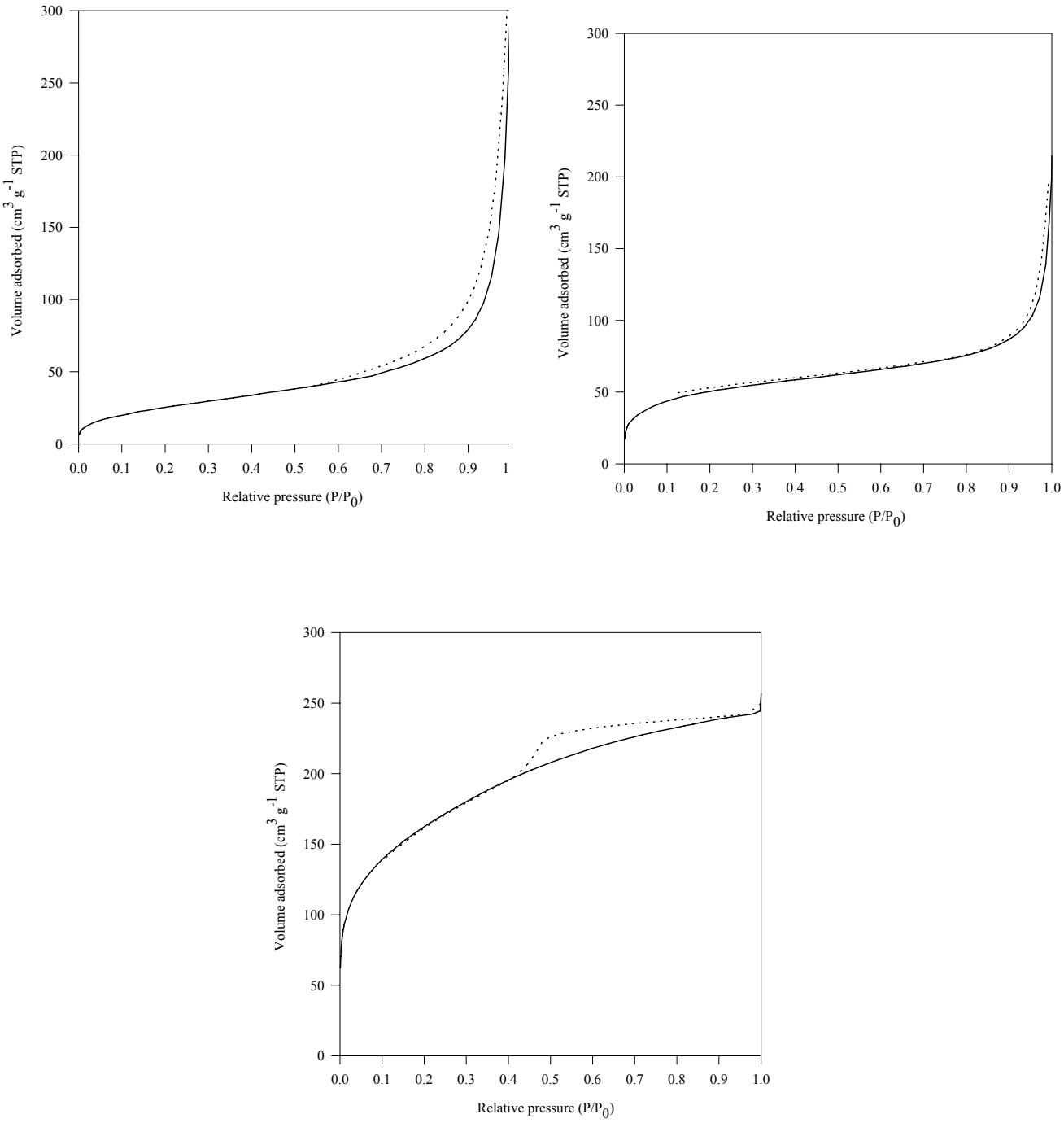

Figure 1S. Isotherm profiles of Fe-MINT (left), Fe-NT (right) and Cu-MINT (bottom).

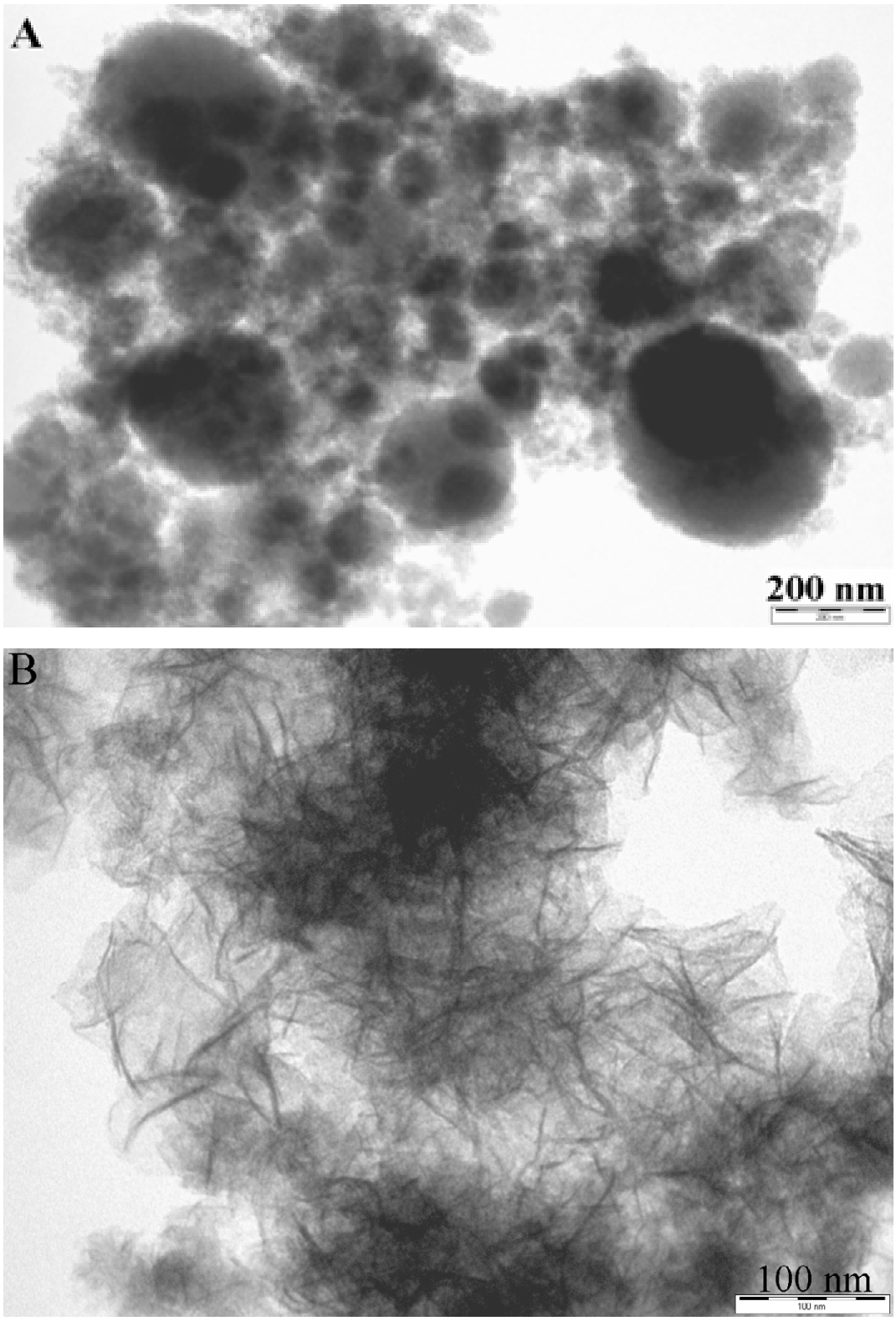

Figure 2S. TEM micrographs of materials prepared under A) under microwave irradiation (200 W, 60-100^{o}C, 15 min) in the absence of metal precursor compared to B) Fe-NT (after 2 h heating at 70ºC) prepared using $FeCl_2$.

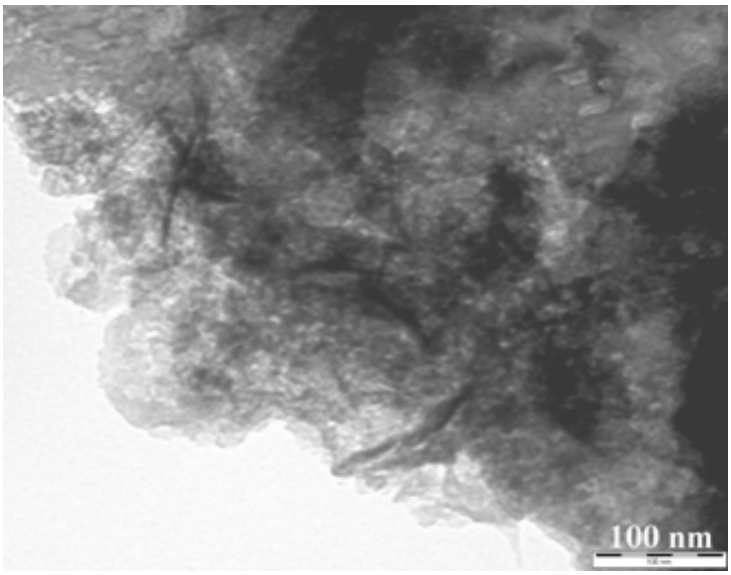

Figure 3S. TEM micrographs of Co-NT prepared using cobalt chloride as precursor.

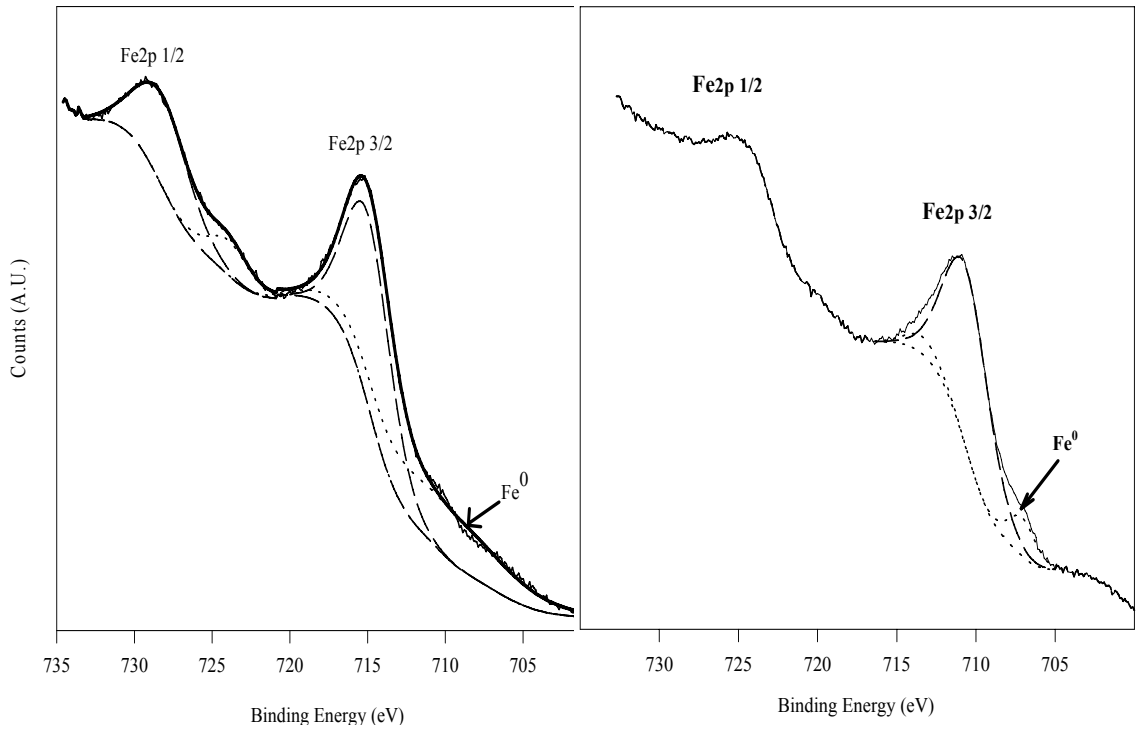

Figure 4S. Fe 2p XPS spectra of Fe-MINT (left) and Fe-NT (right) showing relatively similar Fe^0 content in the materials (slightly lower in Fe-NT 6% compared to a 14% in Fe-MINT) that correlate well with the comparably developed nanotubes in both Fe materials.

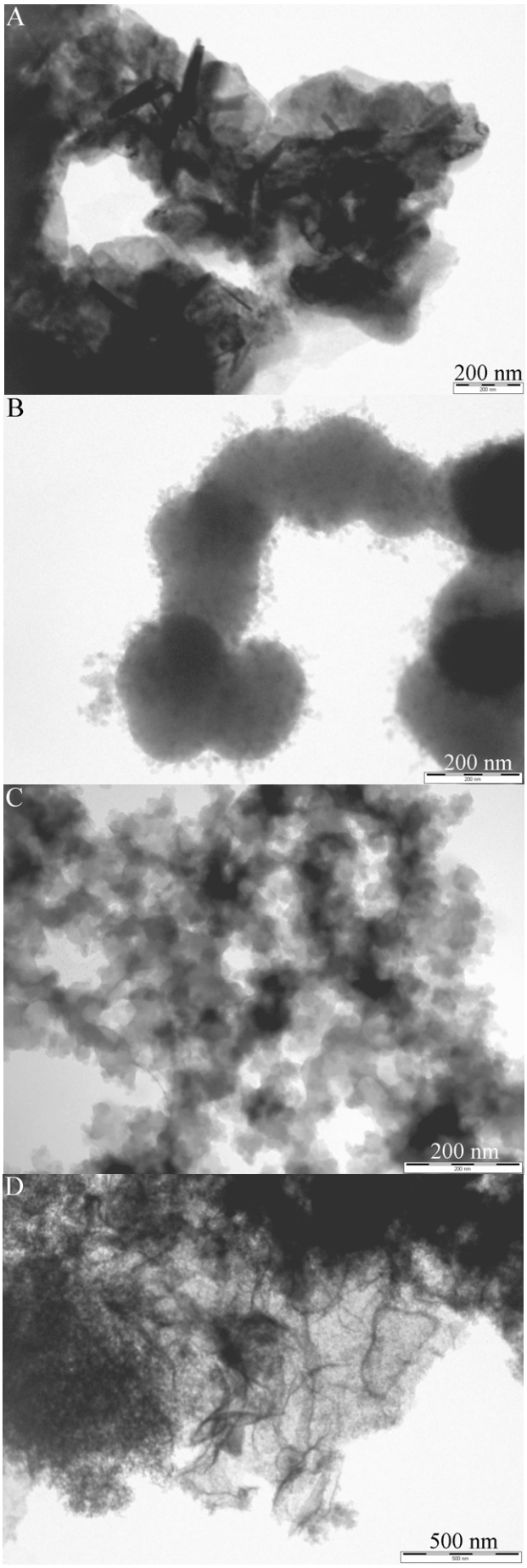

Figure 5S. TEM micrographs of A) $CuBr_2$; B) $Cu(NO_3)_2$; C) $CuSO_4$ and D) CuI prepared materials under conventional heating.

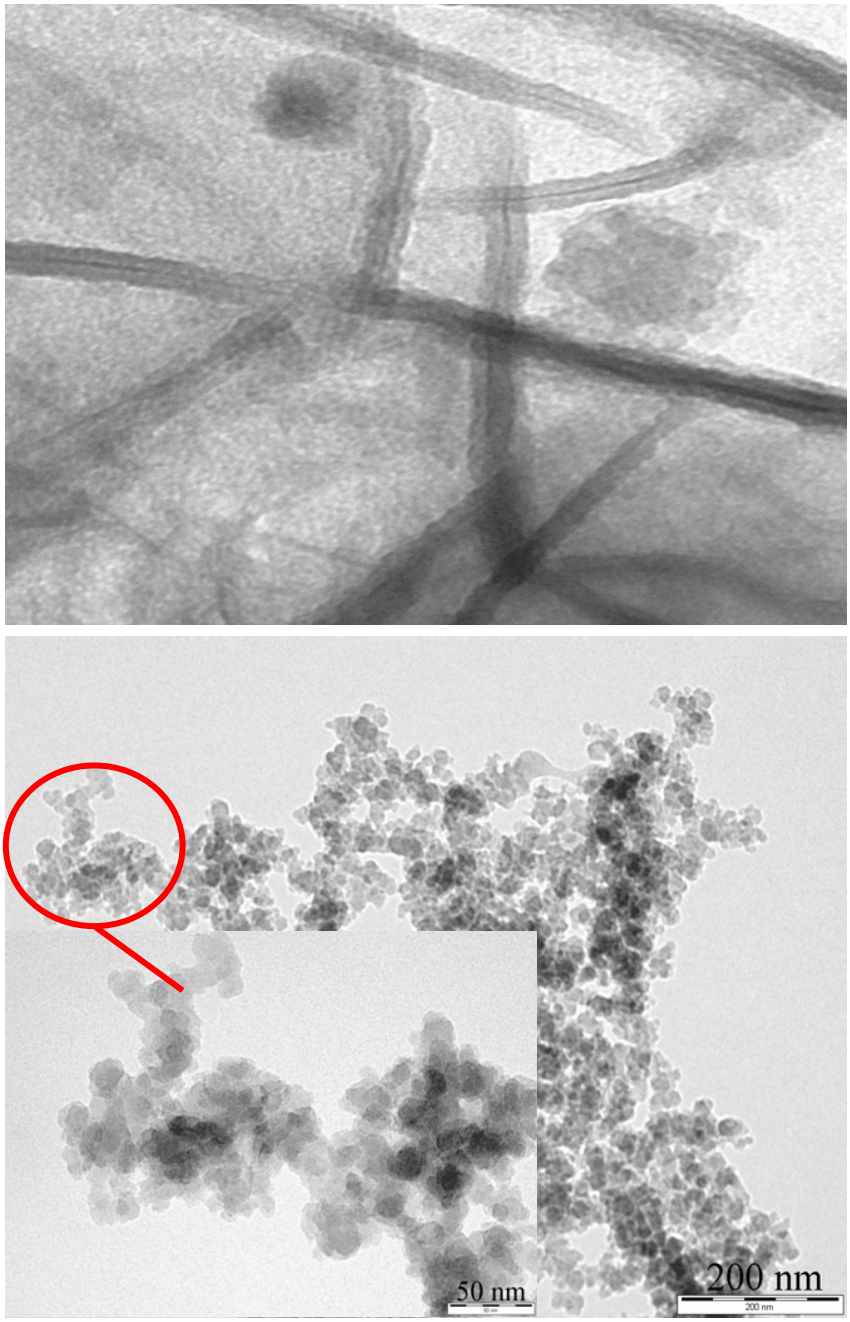

Figure 6S. TEM images of a 0.5%Cu-MINT prepared under microwave irradiation using $CuCl_2$ (top) and Cu acetate (bottom) as metal precursors.

References

[1] C.C. Chusuei, M.A. Brookshier, D.W. Goodman, *Langmuir* 1999, **15**, 2806-2808.

[2] V. Budarin, J.H. Clark, V. Budarin, J.H. Clark, J.J.E. Hardy, R. Luque, K. Milkowski, S.J. Tavener and A.J. Wilson, *Angew. Chem. Int. Ed*., 2006, **45**, 3782-3786.