Spontaneous Self-organization of Cu_2O/CuO Core-shell Nanowires from Copper Nanoparticles

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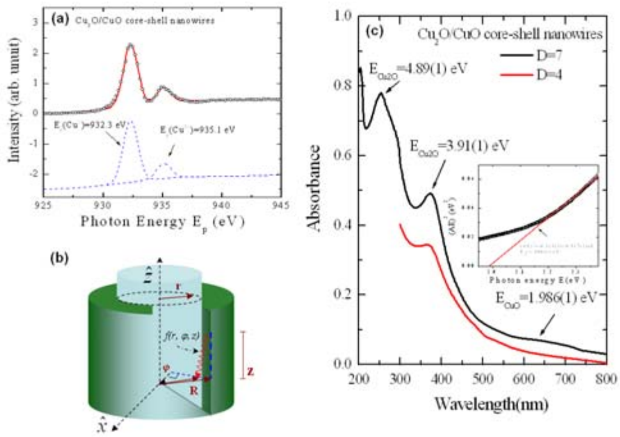
We report on the formation and spontaneous self-organization of Cu_2O/CuO core-shell nanowires from individual copper nanoparticles. The growth process is interpreted using the results of time dependent *in situ* x-ray diffraction. High-resolution transmission electron microscopy is used to observe the intermediate state of pearl necklace-like aggregates that form a chain-like configuration of Cu_2O nanoparticles intertwined into nanowires. The existence of an amorphous CuO shell is confirmed by the XANES technique and explained through an intensity simulation using a proposed core-shell nanowire model.

In the present study [1], we report on a simple method for bottom-up fabrication by means of template-free growth of high density Cu_2O/CuO core/shell nanowires. Spontaneous self-assembly occurs due to the oxidation of ultra-small copper nanoparticles simply by being immersed in ethyl alcohol. This leads to the formation of Cu_2O/CuO core/shell nanowires. The nanosize growth effects of these nanowires are observed experimentally. We find that the formation of nanowires may be far more due to chemical reactions than has previously been realized. XANES spectroscopy of Cu $L_{2,3}$–edge was performed using the 6-m HSGM beam-line (BL01C1) of the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. The photon energies were calibrated with an accuracy of 0.1 eV using the Cu L_3 white line at 931.2 eV of a CuO reference. The recorded spectra were corrected for the energy dependent incident photon intensity as well as for self-absorption effects and normalized to the tabulated standard absorption cross sections in the energy range of 900-1020 eV for the Cu L-edge. The observed spectrum of the energy dependency of the intensity is shown in Fig. 1(a). This result can be understood as due to the occurrence of amorphous CuO and crystalline Cu_2O on the surface and core, respectively. The main peak of Cu $2P_{3/2}$ at 932.3 eV reveals the presence of Cu_2O phase. It is accompanied by a second peak at 935.1 eV related to the CuO phase, and can be regarded as characteristic of Cu^+ and Cu^{2+} ($2p_{3/2} \rightarrow 3d$), respectively. Based on earlier reports of a spherical system , we use as a model a single core-shell nanowire with an inner crystalline Cu_2O core coated by a thin amorphous CuO surface layer (Fig. 1(b)). We use different values of R_1 and R_2 to fit the ratio of I_{Cu2O}/I_{CuO}. These can be obtained from the data. The intensity ratio of the Cu_2O core and CuO shell is thus determined by integrating the peak intensity I_{Cu2O}/I_{CuO}=4.103. All the parameters are allowed to vary simultaneously. Refining processes are carried out until the results meet the ratio of I_{Cu2O}/I_{CuO} obtained from XANES. They are consistent with the TEM and SEM results. The UV–vis absorption spectrum (PerkinElmer Lambda 750) of the Cu_2O/CuO core-shell nanowires is found in order to resolve the excitonic or interband transitions of the Cu_2O core and CuO shell nanocrystals. The two peaks at about 253.5 and 353 nm correspond to the band-to-band transition in Cu_2O nanocrystals. Figure 1(c) shows the curves for both D=7 (black curve) and D=4 (red curve) for comparison. A broad absorption peak centered at about 625.3 nm is observed at D=7. It is found that the growth of the Cu_2O core is confined and terminated by the CuO shell. In the absence of D=7, a CuO shell is obtained. The equation below can be used to obtain an estimate of the optical band gap for a semiconductor. The band gap of the samples is estimated to be E_g=1.986(1) eV (inset to Fig. 1(c)). There is a significant blue-shift compared with that of the reported value for bulk CuO (E_g =1.85 eV). The increase in the band gap of the CuO nanocrystals is indicative of the quantum size effects for semiconductors as the thickness (~ 4.5 nm) becomes comparable to the thermal de Broglie wavelength (~ 6 nm) of a charge carrier.



[1] J.-Y. Ji *et. al.*, Nanotechnology **21**, 045603 (2010).