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Controlling the nanomorphology of thin conformal Cu_2S overlayers grown on Cu_2O compact layers and nanowires

Ignacio Mínguez-Bacho,[a] Marc Courté,[a] Chen Shi,[a] and Denis Fichou*[a,b,c]

[a] *School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore.*

[b] *Sorbonne Universités, UPMC Univ Paris 06, UMR 8232, Institut Parisien de Chimie Moléculaire, F-75005, Paris, France. Tel: +33144275080*; E-mail: denis.fichou@upmc.fr

[c] *CNRS, UMR 8232, Institut Parisien de Chimie Moléculaire, F-75005, Paris, France*

Abstract

Thin conformal Cu_2S overlayers are grown on Cu_2O compact layers (CLs) and nanowires (NWs) by ion exchange reaction (IER). This method is based on the exchange of O^{2-} into S^{2-} ions at the surface of Cu_2O in a solution-containing Na_2S acting as the sulphur ions source. The Cu_2S overlayers are grown under different experimental conditions by varying the Na_2S concentration and the duration of the IER process, thus leading to different Cu_2S nanomorphologies. In particular, when a concentration of 2 mM Na_2S is used, hexagonal Cu_2S nanocrystals are formed on the surface of both Cu_2O CLs and NWs. These nanocrystals are of larger size at the ridges of the Cu_2O cubes in CLs and at the tips of Cu_2O in NWs. The high-quality crystal structure and composition of Cu_2S are confirmed by high resolution transmission electron spectroscopy and X-ray photoluminescence spectroscopy.

Keywords: *Ion exchange reaction; nanomorphology; overlayer; copper oxide; copper sulfide.*

1. Introduction

Nanostructured metal chalcogenides are attracting considerable attention due to their exceptional physical and chemical properties [1, 2]. Applications of these materials are as diverse as thermoelectrical systems, memories, energy conversion, and energy storage devices [3]. Cu_2S is a typical metal chalcogenide behaves is a p-type semiconductor with an indirect band gap E_g=1.2 eV. Depending on the preparation method, Cu_2S thin films can adopt variety morphologies such as nanowires [4], nanocages [5] or nanoparticles with different geometries [6]. Nanostructured Cu_2S is used in lithium ion batteries [7], quantum dots solar cells as counter-electrodes [8] or photovoltaic devices [9]. Cu_2S can be prepared by atomic layer deposition [10], physical vapor deposition [11] or hydrothermal [12], among others.

Together with several other metal oxides [13-15] cuprous oxide Cu_2O is a promising material for photoelectrochemical (PEC) solar energy conversion [16]. In this work we report the preparation and nanomorphology of thin conformal Cu_2S overlayers grown on Cu_2O compact layers (CLs) and nanowires (NWs). The Cu_2S overlayers are grown via an ion exchange reaction (IER) consisting in the exchange of oxygen ions from Cu_2O with sulfur ions from Na_2S contained in an aqueous solution. The nanomorphology of the Cu_2S overlayers can be precisely controlled by adjusting the Na_2S concentration and the IER reaction time, and is independent of the starting Cu_2O morphology, either CLs or NWs.

2. Materials and methods

Cu_2O nanostructures are fabricated as CLs by electrodeposition (see Electronic Supplementary Material ESM†, Section 1.1) and as NWs by anodization (ESM† Section 1.2). Then Cu_2O CLs and NWs (Fig. S1) are used for growing Cu_2S overlayers by IER. Different Cu_2O samples are immersed in 2 mM and 5 mM Na_2S solutions during different times at 80 °C (ESM†, Section 1.3). All materials are analyzed by scanning electron microscopy (SEM, Jeol JSM-6700F) and high-resolution transmission electron microscopy (HR-TEM, JEM-2010). The HR-TEM analysis is carried out on the samples in powder form. Absolute ethanol is added to the powder in a 10 ml bottle and deposited three drops at intervals of 5 minutes on copper grids. X-ray photoelectron spectroscopy (XPS) was performed under monochromatic Al Kα radiation (hv=1486.7 eV) was used at 300 W, 14 kV under ultra-high vacuum.

3. Results and discussion

3.1 Morphology of the Cu_2S overlayers

When carried out during 15 minutes in a 2 mM solution, the IER growth of Cu_2S is slow (Fig 1a,b). It induces the formation of a homogeneous layer of nanostructured Cu_2S crystals all over the surface of the Cu_2O CLs (Fig. 1a). The Cu_2S nanocrystals grow preferentially on the ridges of the cubic Cu_2O structures (Fig. 1b,c). These crystals are of larger size than those growing on the faces of the Cu_2O cubes (Fig. 1d). As expected the Cu_2S nanocrystals are hexagonal in shape. A longer IER duration time up to 60 minutes does not affect drastically the morphology of the Cu_2S overlayer (Fig. 1e), although a thickening of the Cu_2S crystals on the ridges progressively takes place due to an increasing overlap of the crystals (Fig. 1f). Besides, when the Na_2S concentration is increased up to 5 mM, the Cu_2S growth kinetics is faster and takes place in only 2 minutes (Fig. 1g). The Cu_2S overlayer is also very homogeneous, although there are no nanostructures formed on the surface (Fig. 1h,i). A perpendicular cross-arrangement of the constitutive Cu_2S nanocrystals is clearly observed that is similar to that observed in a 2 mM Na_2S solution after 15 minutes (Fig. 1d). Finally, when Cu_2O is immersed in a 2 mM solution, adhesion of the Cu_2S overlayer on Cu_2O CLs is excellent, thus making potential applications realistic. However, we note that adhesion of the Cu_2S overlayer is reduced when using a higher Na_2S concentration of 5 mM, thus leading to partial detachment of the Cu_2S overlayer.

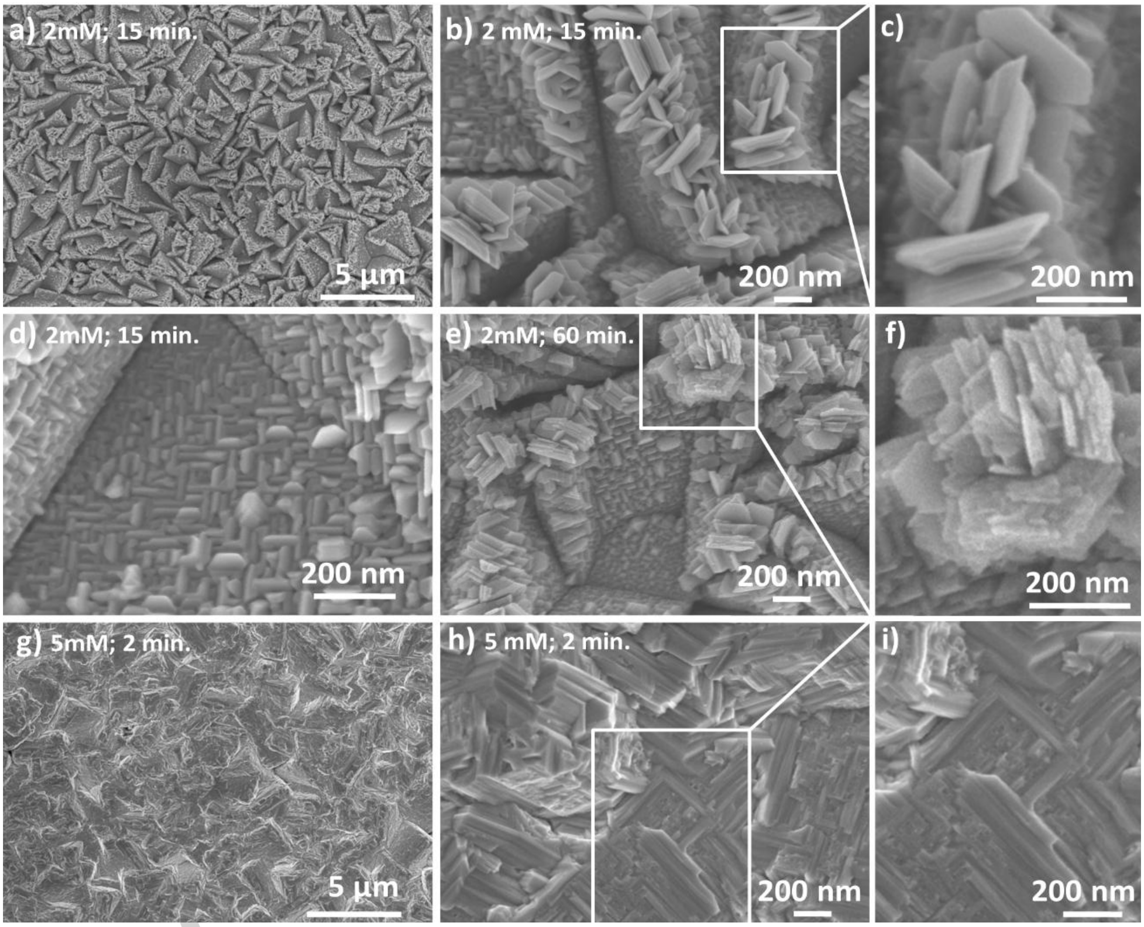

Fig. 1 SEM micrographs of Cu_2O compact layers (CLs) coated with a Cu_2S overlayer prepared by IER under different Na_2S concentrations and reaction times. Magnifications of the Cu_2S nanocrystals inside the white squares are shown on the right images.

IER has been also conducted on Cu_2O NWs in solutions containing Na_2S concentrations of respectively 2 mM and 5 mM. After 30 minutes of IER in a 2 mM solution an overlayer of Cu_2S nanocrystals grows around the NWs (Fig. 2a). The morphology of the Cu_2S layer (Fig. 2b) is comparable to that obtained in similar conditions on CLs (Fig. 1b,e). Noticeably, larger Cu_2S

nanostructures grow on the Cu_2O NWs tips, a phenomenon which is reminiscent of the higher concentration of Cu_2S nanocrystals on the Cu_2O CLs ridges (*vide supra*). On the other hand, when the IER process is carried out in a 5 mM solution, the Cu_2S overlayer is not nanostructured (Fig. 2c) although the Cu_2S crystal structure formed after 5 minutes is still visible (Fig. 2d). This morphology resembles that of the Cu_2S-coated Cu_2O CLs grown into a 5 mM solution (see Fig. 1h,i). However, in contrast to Cu_2S overlayers grown on CLs using a 5 mM Na_2S concentration, the Cu_2S overlayers grown on NWs in 5 mM solutions exhibit a very good adhesion to Cu_2O.

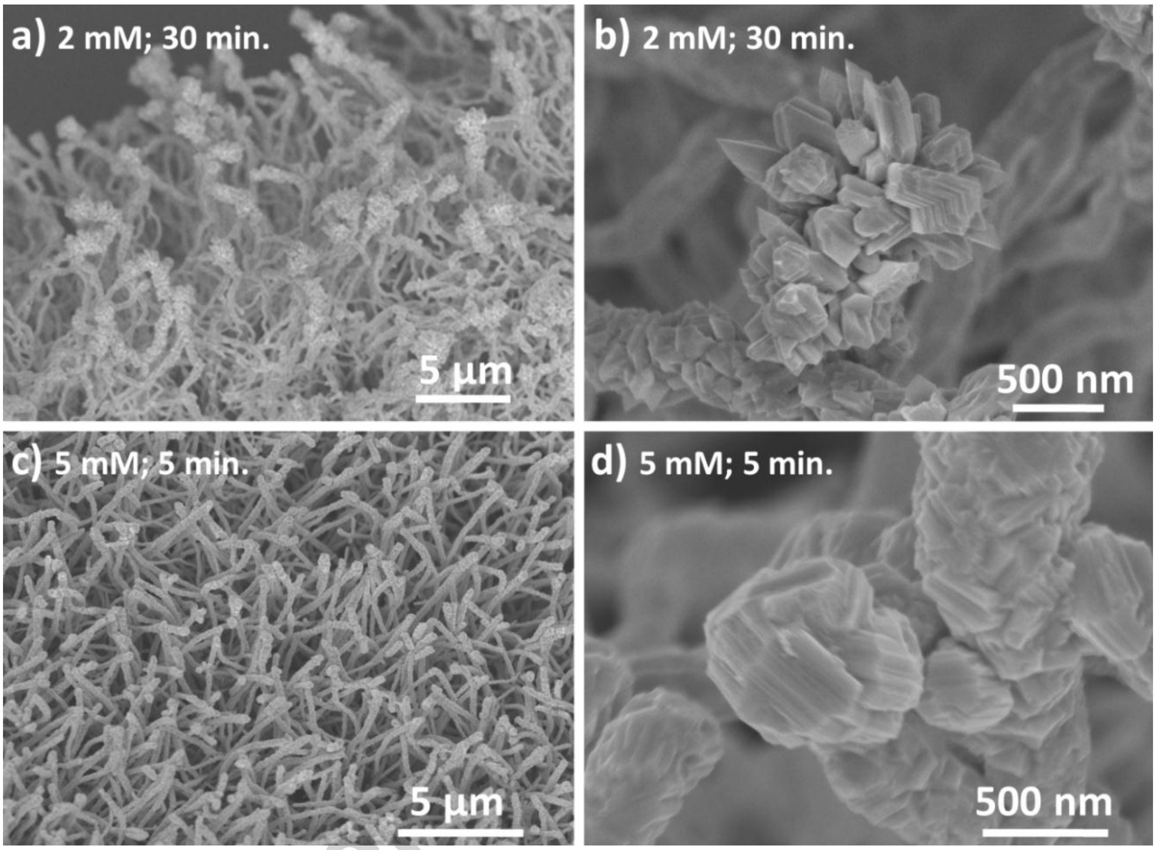

Fig. 2 SEM micrographs of Cu_2O nanowires (NWs) coated by a Cu_2S overlayer prepared an IER process under different Na_2S concentrations and reaction times.

3.2 High resolution transmission electron microscopy (HR-TEM)

Images in Fig. 3a,b correspond to Cu_2S-coated Cu_2O samples for respectively a CLs and NWs. In both images dark and bright areas are observed. The selected regions delimited by white squares are analysed by fast Fourier transform (FFT). Fig. 3c represents the FFT performed in the selected region of the brighter area of a CL. It reveals lattice spacing of 3.19, 2.78 and 1.96 Å which can be attributed to the (111), (200) and (220) planes of Cu_2S. In the FFT of the selected region in darker area (Fig. 3d), three lattice spacing of 2.45, 2.13 and 1.50 Å are observed that can be attributed respectively to the crystallographic planes (111), (200) and (220) of Cu_2O. The FFT analysis of the bright selected area of the NWs (Fig. 3e) reveals an interplanar distance of 1.96 Å corresponding to the (220) plane of Cu_2S. It also unveils the (200) plane corresponding to Cu_2O with a interplanar distance of 2.13 Å. The crystallographic planes of Cu_2O are also observed very clearly in the FFT of the region in the darker area (Fig. 3f).

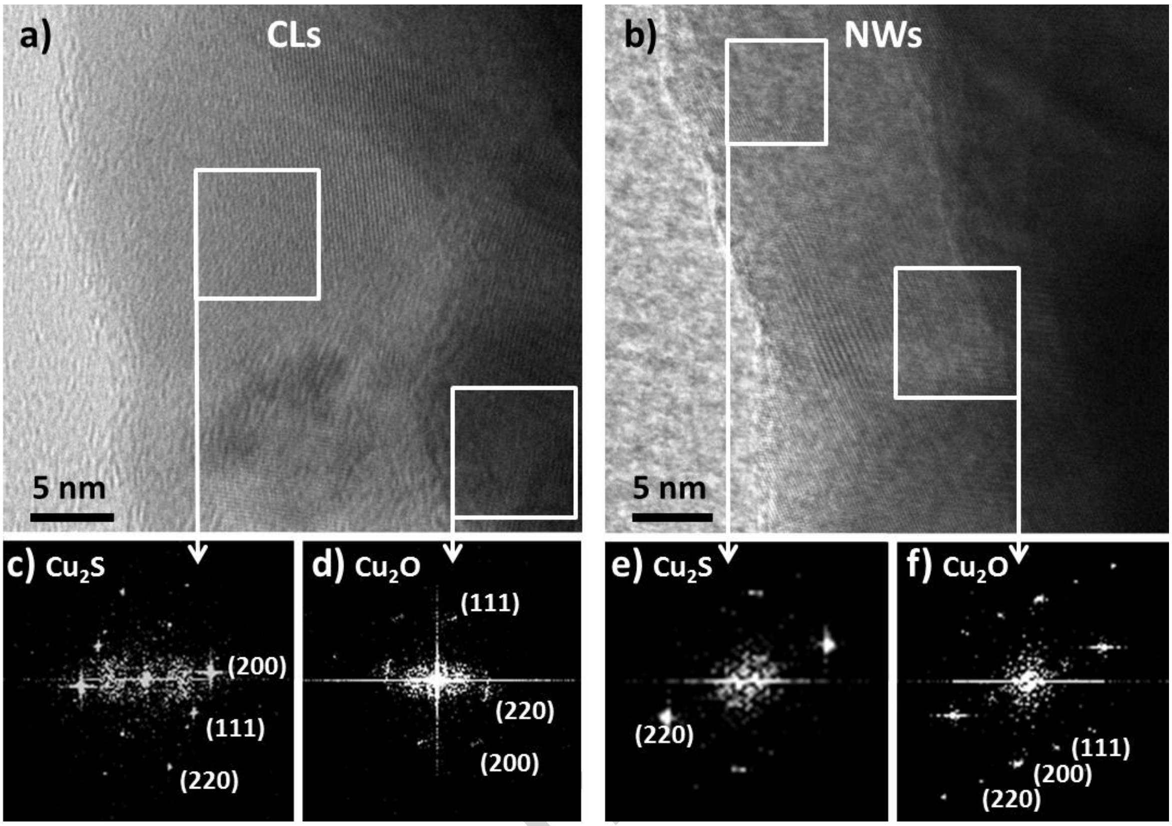

Fig. 3 HR-TEM images of Cu_2S-coated Cu_2O a) CLs and b) NWs. c,d,e,f) FFT analysis of the selected regions in either dark or bright contrast (white squares)

3.3 X-ray photoluminescence spectroscopy (XPS)

We performed X-ray photoelectron spectroscopy (XPS) in order to confirm the formation of Cu_2S (Fig. 4). In the wide XPS spectra are shown the Cu 2p, Cu LMM, O 1s, C 1s and S2p for both CLs and NWs (Fig. 4a,b). We can observe the Cu $2p_{1/2}$ peak at 952.5 eV and the Cu $2p_{3/2}$ peak at 932.6 eV (Fig. 4c) showing that the oxidation state of copper species correspond to Cu^+. We have seen no satellite peaks of Cu $2p_{1/2}$ and Cu $2p_{3/2}$ which is an evidence of the absence of Cu^{2+} oxidation state on the surface of the overlayers on CLs and NWs. For both CLs and NWs the S 2p regions (Fig. 4d) show the characteristic shape of an S^{2-} band. Peaks at 162.9 eV and 161.8 eV can be attributed to the S $2p_{1/2}$ and S $2p_{3/2}$ spin-orbit doublet.

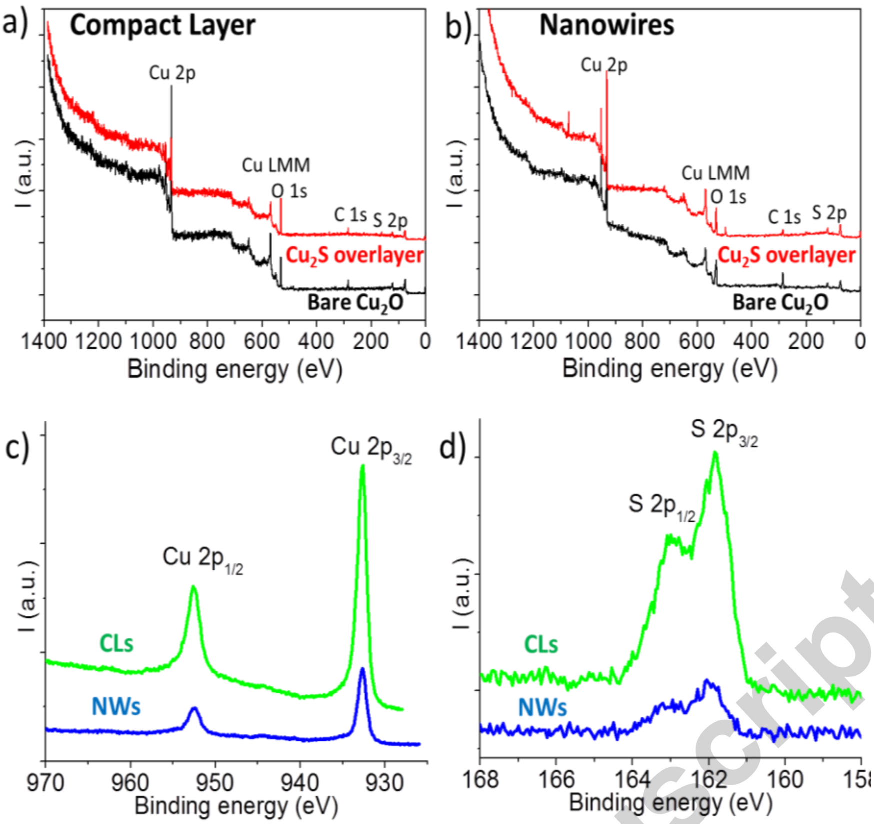

Fig. 4 a,b) Wide scan XPS spectra of Cu_2O CLs and NWs with (red) and without (black) Cu_2S overlayers. c,d) XPS spectra of the Cu2p and S2p regions of the Cu_2S overlayers on CLs (green) and NWs (blue).

4. Conclusion

The influence of the concentration of Na_2S solution is a critical parameter for the growth of the Cu_2S overlayers on Cu_2O compact layers and nanowires by ion exchange reaction. When a concentration of 2 mM Na_2S is used, hexagonal Cu_2S nanocrystals are formed on the surface of both Cu_2O CLs and NWs. The sizes of the crystals are bigger at the ridges of the Cu_2O cubes in CLs and the tips of Cu_2O in NWs. The time scale of the IER process does not affect much the Cu_2S morphology although larger clusters of Cu_2S nanocrystals are formed at the ridges of the CLs. HR-TEM confirms the formation of the Cu_2S single crystals while XPS reveals the high-quality chemical composition of the overlayers. We are presently using these conformal Cu_2S overlayers to protect Cu_2O electrodes during photoelectrochemical experiments that will be reported elsewhere [17].

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Highlights

- Conformal layers of Cu_2S on Cu_2O are grown by ion exchange reaction.
- The morphology of the Cu_2S overlayers is not dictated by the morphology of the starting Cu_2O material.
- Different Cu_2S nanomorphologies are studied by SEM, HRTEM and XPS.
- Cu_2S overlayers have a potential application as protection against photodecomposition of Cu_2O photoelectrodes.