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Evidence of nanosized copper anodic reaction in anaerobic sulfide aqueous solution

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Abstract

The present paper reports the use of TEM to investigate the electrochemical behavior of copper subject to the both free corrosion and polarization in 0.1 M NaCl + 5×10^{-4} M Na₂S aqueous solution at nano scale. The pure copper is found to be transformed into nano-crystalline Cu₂S in the thin region of copper needle in the solution at open circuit condition. However, rough Cu₂S layer is formed in the active region of electrochemical polarization, which is then converted to the passive CuS layer with uniform thickness at higher potentials. Upon the continuous increase of applied potential, cubic CuS particles with the size of ~ 100 nm are precipitated on the needle surface due to the breakdown of passive layer. Meanwhile, the growth of a large amount of nanosized CuCl particles is also found, indicating that Cl⁻ ions participate in the electrochemical reaction in the transpassive region. It is worth to note that the present work also provides a simple and cost-effective way for the synthesis of copper sulfides (Cu₂S and CuS) through electrochemical processes.

Keywords: copper, sulfide solution, sulfuration, TEM

Introduction

Copper, one of the most widely used metals, has been employed in various fields for thousands of years due to its excellent mechanical properties, such as great ductility, high thermal and electrical conductivity. However, corrosion tends to occur on copper easily when it is exposed to corrosive environments. The understanding of film growth on copper under natural immersion as well as the electrochemical conditions is of great importance for various applications in chemistry and electrochemistry.

The corrosion resistance of copper to sulfide ions has been broadly studied since copper is an important material in repository and cooling systems, where SH^- ion exists with very low concentration in the surrounding atmosphere.^{1, 2} Most of the previous studies focused on the corrosion behaviors of copper in anaerobic sulfide solutions through long-term immersion.^{1, 3-7} It is widely accepted that a single cellular Cu_2S (Chalcocite) film will grow on the copper surface after being immersed in sulfide solution with the presence of chloride ions. However, linear and non-linear growth of the films on copper was found in sulfide solutions with different concentrations,^{3, 4} since the mechanism of the initial state of the film growth is still not so explicit due to the difficulty in characterizing the thin layer. In addition to the immersion studies, electrochemical methods have also been performed to investigate the film growth of copper in aqueous solutions with the presence of sulfide ions.⁸⁻¹³ Based on these studies, Cu_2S is still regarded as the main composition of the corrosion layer while CuCl may appear in the corrosion film during the anodic process. Besides, CuS is another possible product that has not been proved yet.^{10, 14} To make better understanding of the film growth process and the corrosion products, powerful technologies are necessary to enable

us to observe the morphology of the thin layer in high magnifications and characterize their compositions.

Transmission electron microscopy (TEM) is a powerful technique, which has the capability of characterizing oxidation layer on copper¹⁵ and even thinner passive film on nickel¹⁶ at nano scale. In the present paper, copper needle specimen was fabricated initially, followed by short-term immersion and then electrochemical polarization in anaerobic sulfide solutions. Subsequent examination of the corroded copper needle was performed using TEM. The evidence of electrochemical behavior of copper needle subject to sulfide aqueous solution has been successfully collected. In addition, the present work also provides a way for the synthesis of copper sulfides (Cu_2S and CuS) through electrochemical processes. Metal sulfides have been drawn special attention due to their promising potentials in various fields, such as energy storage,¹⁷⁻²⁴ bio-sensing,²⁵⁻²⁸ catalysis²⁹⁻³¹ et al.

It is known that selected area electron diffraction (SAED) pattern generated in TEM is a normal technique to identify/verify the lattice structure of a crystalline material. But it is imposed by the size of the selected area aperture, which only enables a minimum area of a circle with a diameter of $\sim 10 \mu\text{m}$ to be examined. However, Fast Fourier Transform (FFT) pattern allows the determination of the atomic lattice structure from a small area of the sample at nano scale. An FFT pattern is a reciprocal image taken and transformed from a specific area of a real image (i.e. a high-resolution atomic TEM image). The crystalline structures (such as the lattice cell parameters and crystalline space groups) can be figured out through the process of indexing the FFT pattern, which are characteristics of and unique to a specific material. Table 1 lists crystalline space groups and cell

parameters of Cu_2S , CuS and CuCl .

1. Experimental

The fabrication of copper needles was carried out by using a precise argon ion beam that sputters the grids of pure copper grid (purity 99.99%). A sample holder that mounts a copper grid of 3 mm in diameter was loaded into the chamber in a Gatan 691 precise ion milling system (PIPS) (Gatan, Inc., Warrendale, PA, United States). The detailed fabricating procedure has been reported in our previous work.^{15, 16}

The open-circuit electrochemical oxidation and anodic polarization of copper needles were performed in a N_2 -purged anaerobic chamber with 0.1 M NaCl + 5×10^{-4} M Na_2S aqueous solution at room temperature ($25 \pm 1^\circ$). A typical three-electrode potentiostatic system of AUTOLAB PGSTAT 302N (Metrohm Pte Ltd., Switzerland) was used for the electrochemical measurements. The post-fabricated copper grids were used as the working electrode an Ag/AgCl electrode (3 mol L^{-1} KCl solution) as the reference electrode, and a platinum foil as the counter electrode in the electrochemical cell. All potential values are referenced against the Ag/AgCl electrode in the present work. The polarization was implemented by scanning to three potentials at different regions with a scan rate of 1 mV/s. On completion of the electrochemical experiments, the copper grid was taken out of the cell rapidly followed by rinsing thoroughly with deionized water, and then drying 30 min in a vacuumed desiccator at room temperature. Finally, the sample was transferred into TEM (JEOL JEM-2100F) for observation at an accelerating voltage of 200 keV.

2. Results and discussion

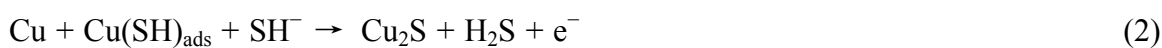
Fig. 1 illustrates the evolution of a copper needle after immersion in 5×10^{-4} M Na_2S + 0.1 M NaCl solution for 72 hours. The as-prepared copper needle has a thin tip region (Fig. 1a), which is electron transparent and identified to be single crystalline as demonstrated from the selection area diffraction pattern (inset in Fig. 1a). It is a sharp spot array and reflected from Cu [1 0 1]. This single crystalline needle tip is completely transferred into corrosion products (Fig. 1b) after 24 hours' dissolution in the solution. These corrosion products present a polycrystalline structure, as indicated from the ring diffraction pattern (inset in Fig. 1b). The thin area in the needle tip is seen to increase when subjected to the attack of 48 hours (Fig. 1c) and 72 hours (Fig. 1d) in the solution. The loss of the top of the needle tip in Fig. 1c is apparently resulted by the fast corrosion and the weaker strength of the corrosion products, which are clearly viewed to be porous and consist of nano-particles from Fig. 1e, a magnified TEM image of the square marked area (A) in Fig. 1d. Fig. 1e shows a high-resolution TEM image taken from the square marked as B in Fig. 1d. The inset is the indexed FFT pattern performed from the square area of C and produced from Cu_2S [0 0 0 1].

Potentiodynamic polarization was carried out to investigate the anodic behavior of copper needle in 5×10^{-4} M Na_2S + 0.1 M NaCl solution. Fig. 2 shows a typical polarization curve obtained from scanning the copper needle from -0.1 V to 0.15 V. During the anodic polarization, the current density increases rapidly between O and A (active region), then at a very slow rate from A to B (passive region) and very fast again

afterwards (transpassive region) with the increase of the potential. The variation of electrochemical behavior that the copper needle performs in the different regions is reflected by the formation of corrosion product layer over its surface. TEM is a tool that allows the direct observation of the morphologies of the corrosion products at nanoscale.

Fig. 3a is bright-field TEM image showing an as-prepared pure copper needle which has a very smooth surface. This surface is then seen to be decorated with a corrosion product layer (Fig. 3b) after the copper needle is subjected to the polarization across the activation region the point A. Uneven and fast corrosion rate on the surface of copper needle over the activation region during the polarization leads to the rough and non-uniform corrosion product layer formed by nanoparticles. Some nanoparticles are the corrosion products that are dissolved into the solution and subsequently redeposited back to the needle surface.⁸ Due to the strong radial converging effect, the corrosion product layer appears much thicker towards the top of the needle tip.

To clarify the phase structure of the corrosion product layer, HR-TEM images (Fig. 3c and 3d) are taken from two typical square regions A and B (Fig. 3b), respectively. Based on the inset FFT pattern converted from square C, hexagonal Cu₂S (Chalcocite) in a projection plane of (2-1-1 0) is identified. Likewise, Cu₂S with the same crystalline structure but at different zone axis [1 0 -1 1] is determined from the FFT pattern that is generated from the square region D in Fig. 3d. The formation of the CuS layer follows the reactions below:⁸



It is worth to note that the crystalline structure of Cu_2S generated during dissolution and electrochemical polarization in the electrolyte is identical since Chalcocite is the most stable structure for Cu_2S at room temperature.¹²

Fig. 4b is the result after the as-prepared copper needle (Fig. 4a) encounters the passive polarization till the point B in Fig. 2. The passivation is a process in which the copper needle undergoes an even dissolution rate leading to the formation of a uniform and compact corrosion product layer as shown in Fig. 4b. This uniform corrosion product layer is determined to be hexagonal CuS (Covellite) phase by the analysis of the reciprocal pattern (inset in Fig. 4c), a HR-TEM image taken from the marked square area (A) in Fig. 4b at $[0\ 0\ 0\ 1]$ zone axis. Some nanoparticles are visible and decorated over the layer surface, which are the redeposited corrosion products from the solution. These nanoparticles are also hexagonal CuS (Covellite) but have a different orientation from the corrosion product layer. As an example, Fig. 4d shows a HR-TEM image taken from the square area B of a nanoparticle (Fig. 4b), which is oriented along $[1\ 1\ -2\ 0]$ zone axis, as indexed from the inset FFT pattern in Fig. 4d. The formation of the CuS layer follows the two paths below:³²



1)



and

2)



Cubic particles with the size of ~100 nm are formed on the surface of the passive layer when the copper needle was further polarized to the transpassive region. A cross-sectional TEM image (Fig. 5a) shows the edge of the copper needle decorated with many cubic nanoparticles, which are also identified to be CuS by using the same method as above. These nanoparticles are seen to be randomly dispersed across the whole surface of the copper needle in Fig. 5b, a plan-view SEM image. The growth of CuS cubic nanoparticles may be attributed to the breakdown of the protective layer followed by the high dissolution of copper into Cu ions which subsequently diffuse towards sulfide solution. When taking a close look at a high magnification SEM image (Fig. 5c), more small nanoscale particles are observed to attach on the surface. They are identified to be cubic CuCl (Nantokite) through the index of the inset FFT pattern performed from HRTEM image (Fig. 5d). This indicates that Cl⁻ ions also involve in the reactions in the transpassive region when the polarization potential is sufficiently high. Based on these findings, new synthesis methods can be invented to fabricate CuS nanoparticles using electrochemical polarization.

According to the results of the electrochemical processes, the estimated formation mechanisms for each species can be presumed. At low potentials, Cu₂S is found to be predominant due to the electroabsorption/ electrodeposition equation (1) and (2), where only the Cu at surface is gently oxidized to form Cu₂S. With the increase of potentials,

Cu₂S layer is not stable enough to be presented in higher potentials and transform into CuS passive layer coherent to the copper substrate via equation (6). When it reaches to the transpassive region, more and more Cu²⁺ can be generated from the copper substrate, then they will diffuse and penetrate the passive film towards the solution so that CuS cubic particles can be obtained via equation (7). At this stage, the rapid interaction between Cu²⁺ and S²⁻ leads to the further consumption of S²⁻, which gives rise to the exposure of excessive Cu²⁺ to the solution with high-concentration Cl ions. As a consequence, Cu²⁺ will have to react with Cl⁻ to form CuCl although S²⁻ has the priority to combine with Cu²⁺. Thus, electrochemical polarization is an effective way to fabricate Cu₂S and CuS products on the copper surface. Based on the estimation of our research results, in the open circuit condition, the yield of Cu₂S is up to 100% subject to the corrosion of a long time (72 hours) at the tip region of the copper needle sample. In contrast, the Cu₂S yields in the active region and passivation region are around 30% (in 1 minute) and 50% (in 2 minutes) of the conversion of the copper in the needle sample's tip area. The yield of CuS in the transpassive region is approximately 10 CuS nanoparticles per 1 μm² in number.

3. Conclusions

In the present work, electrochemical behavior of copper nanoneedle is performed in sulfide solutions with the assistance of TEM. Copper encounters the fast corrosion in in 0.1 M NaCl + 5 × 10⁻⁴ M Na₂S aqueous solution at open circuit condition. Cu₂S nano-crystalline layer with the porous and rough surface is found to form in the active region during electrochemical polarization. Further electrochemical polarization in

passivation region brings about a CuS uniform layer. The continuous increase of the applied potential breaks the passive layer resulting in copper dissolution towards the sulfide solution, leading to the formation of cubic CuS particles on the needle surface. At the same time, CuCl is also formed as a result of the reaction between dissolved copper and chloride ions. Therefore, electrochemical polarization is an effective way to fabricate CuS nanoparticles on the copper surface.

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Table 1. Crystallographic data of Cu₂S, CuS and CuCl

	Crystal system	Cell parameters
Cu₂S	hexagonal	a= 0.395 nm, c= 0.675 nm
CuS	hexagonal	a= 0.380 nm, c= 1.636 nm
CuCl	cubic	a= 0.493 nm

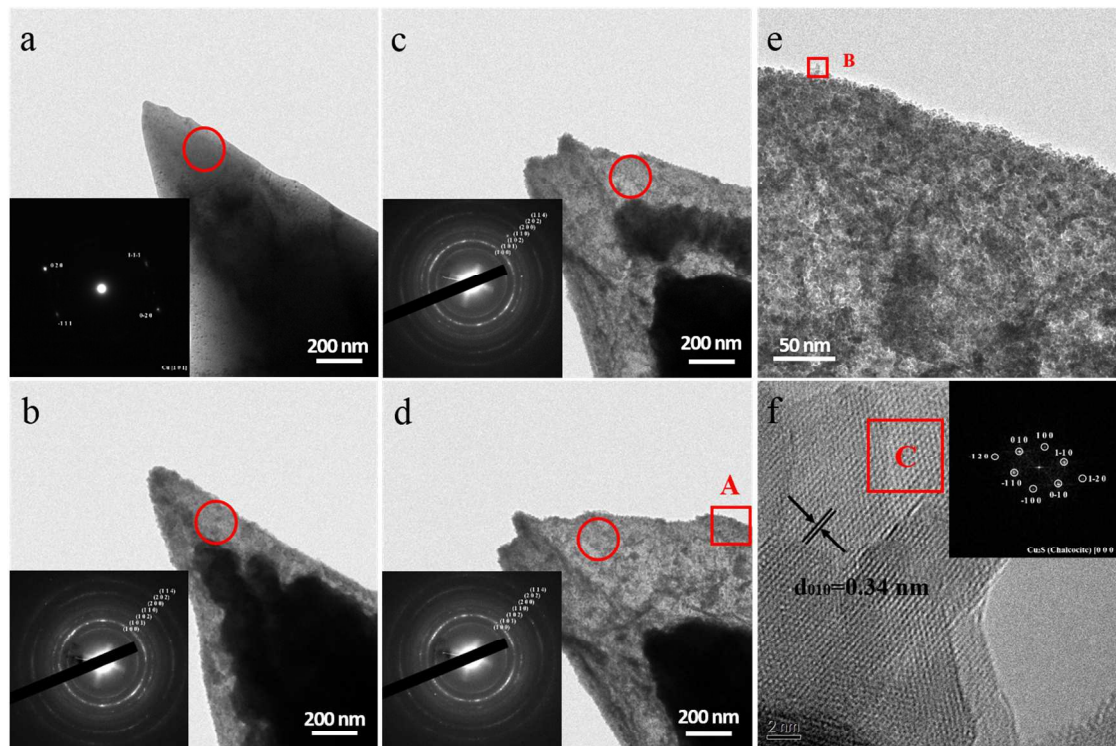


Figure 1. (a)- (d) Bright-field TEM images of a copper needle specimen (with inset FFT patterns of circle region) being immersed in 5×10^{-4} M Na_2S + 0.1 M NaCl solution for 0 hour, 24 hours, 48 hours and 72 hours, respectively; (e) Magnified TEM image of square A in Figure 1d; (f) HR-TEM image of square B in Figure 1e.

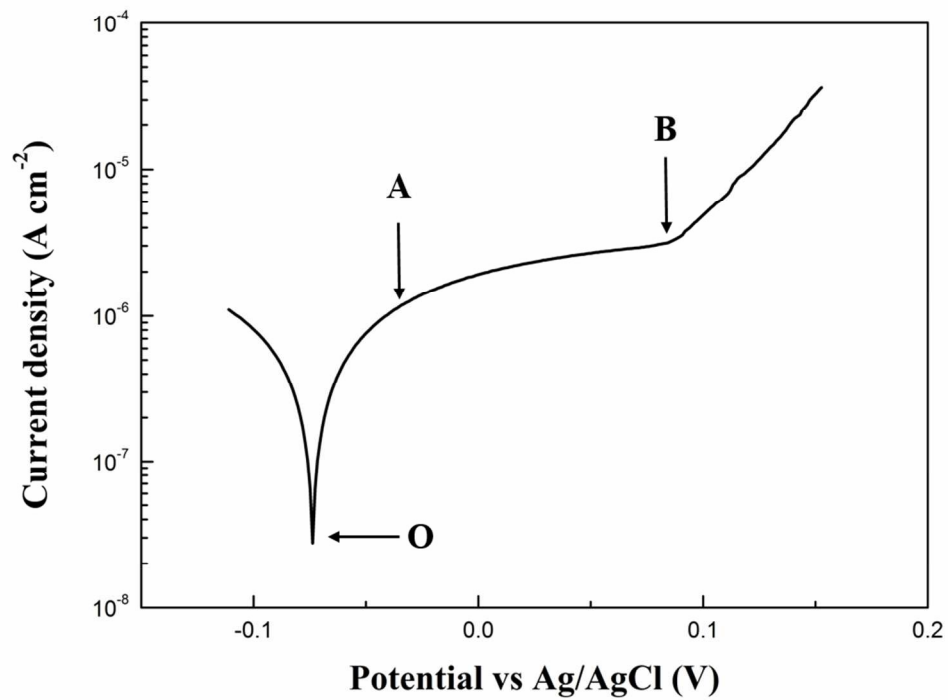


Figure 2. A potentiodynamic polarization curve of copper grid electrode in 5×10^{-4} M Na_2S + 0.1 M NaCl solution

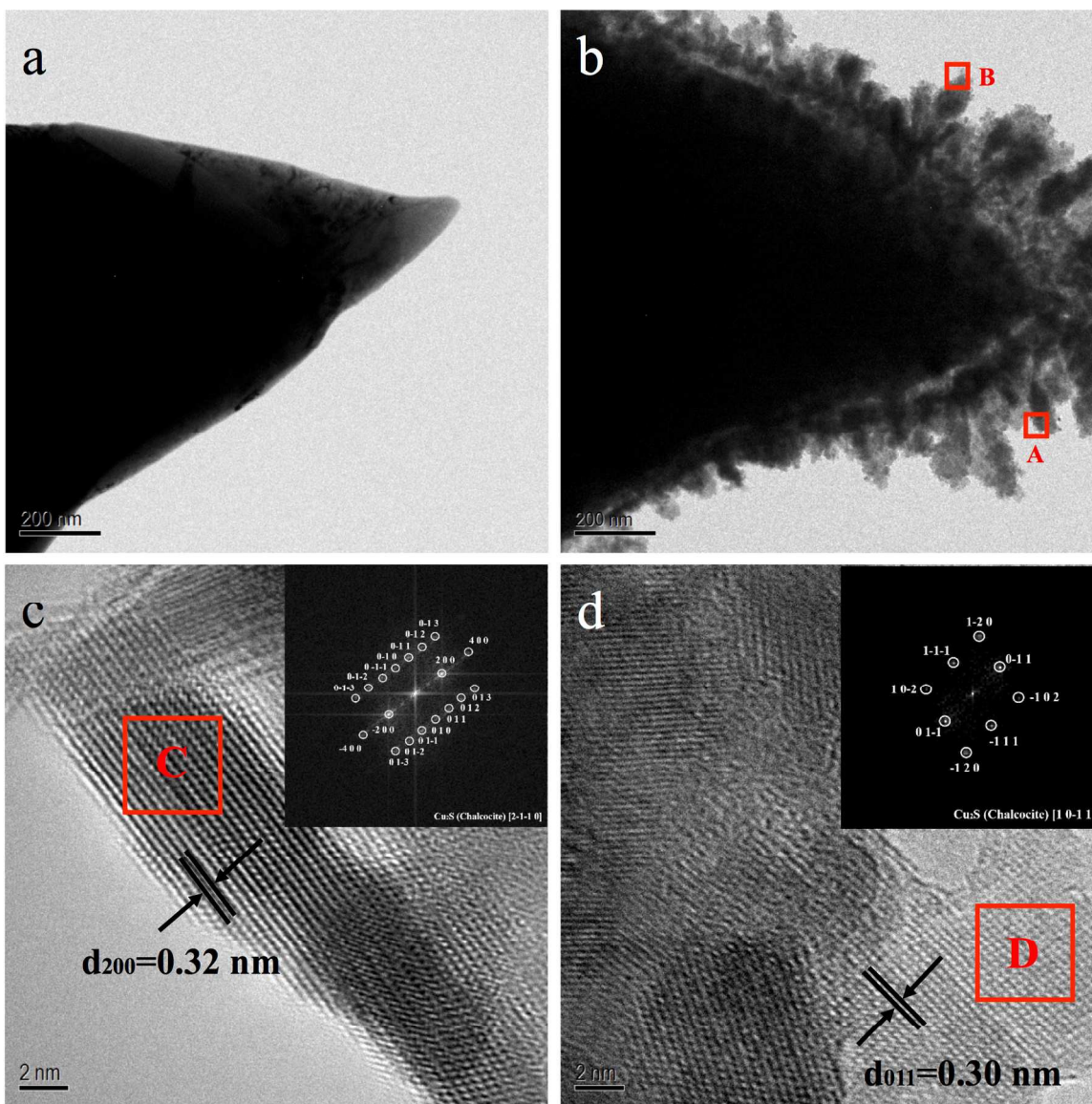


Figure 3. (a), (b) Bright-field TEM images of a copper needle before and after electrochemical polarization to active region in Figure 2, respectively; (c), (d) HR-TEM images of localized regions A and B in (b) and FFT patterns taken from the inset squares, respectively.

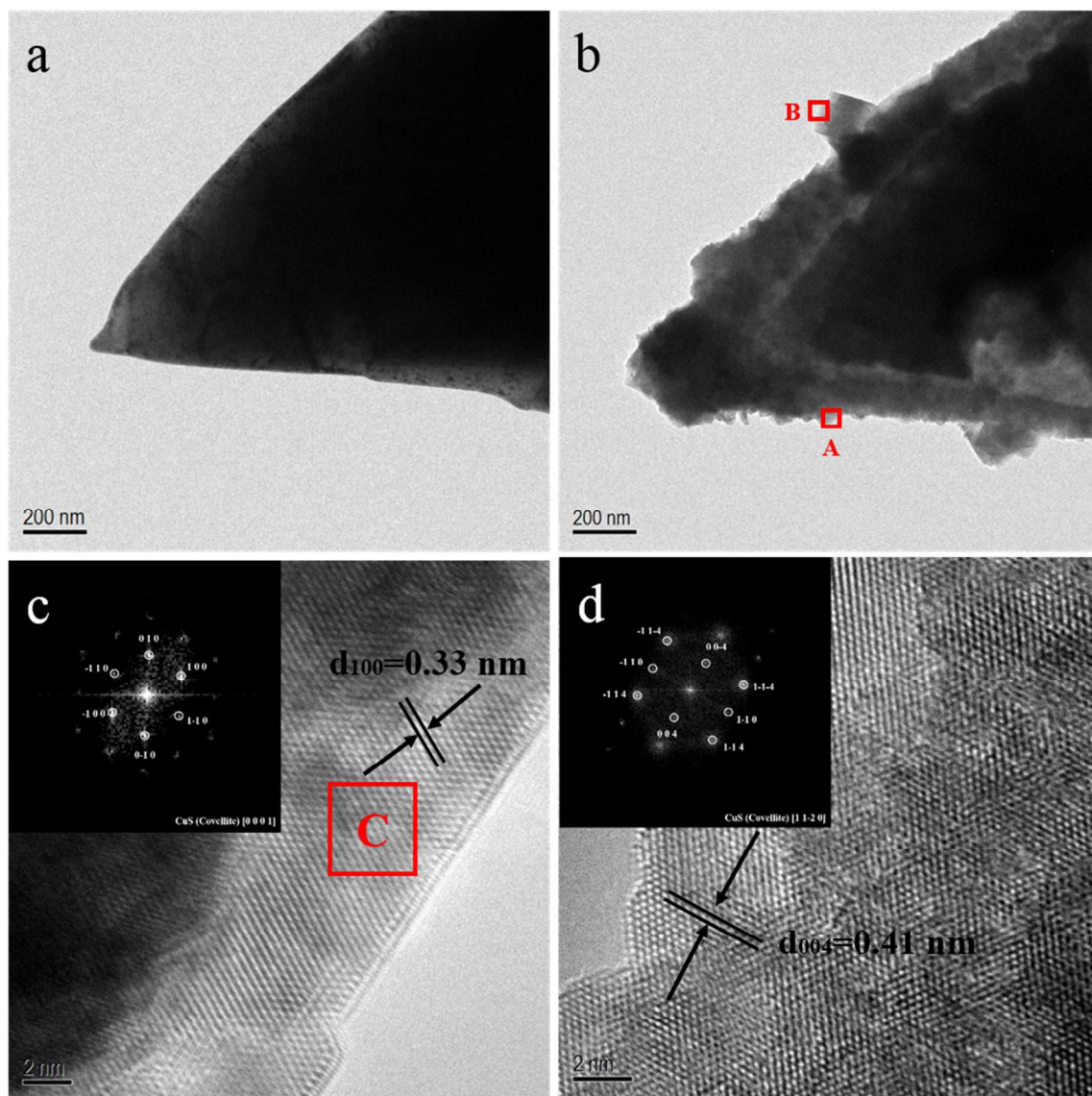


Figure 4. (a), (b) Bright-field TEM images of a copper needle before and after electrochemical polarization to passive region in Figure 2, respectively; (c), (d) HR-TEM images of localized regions A and B in (b) and FFT patterns taken from the inset squares, respectively.

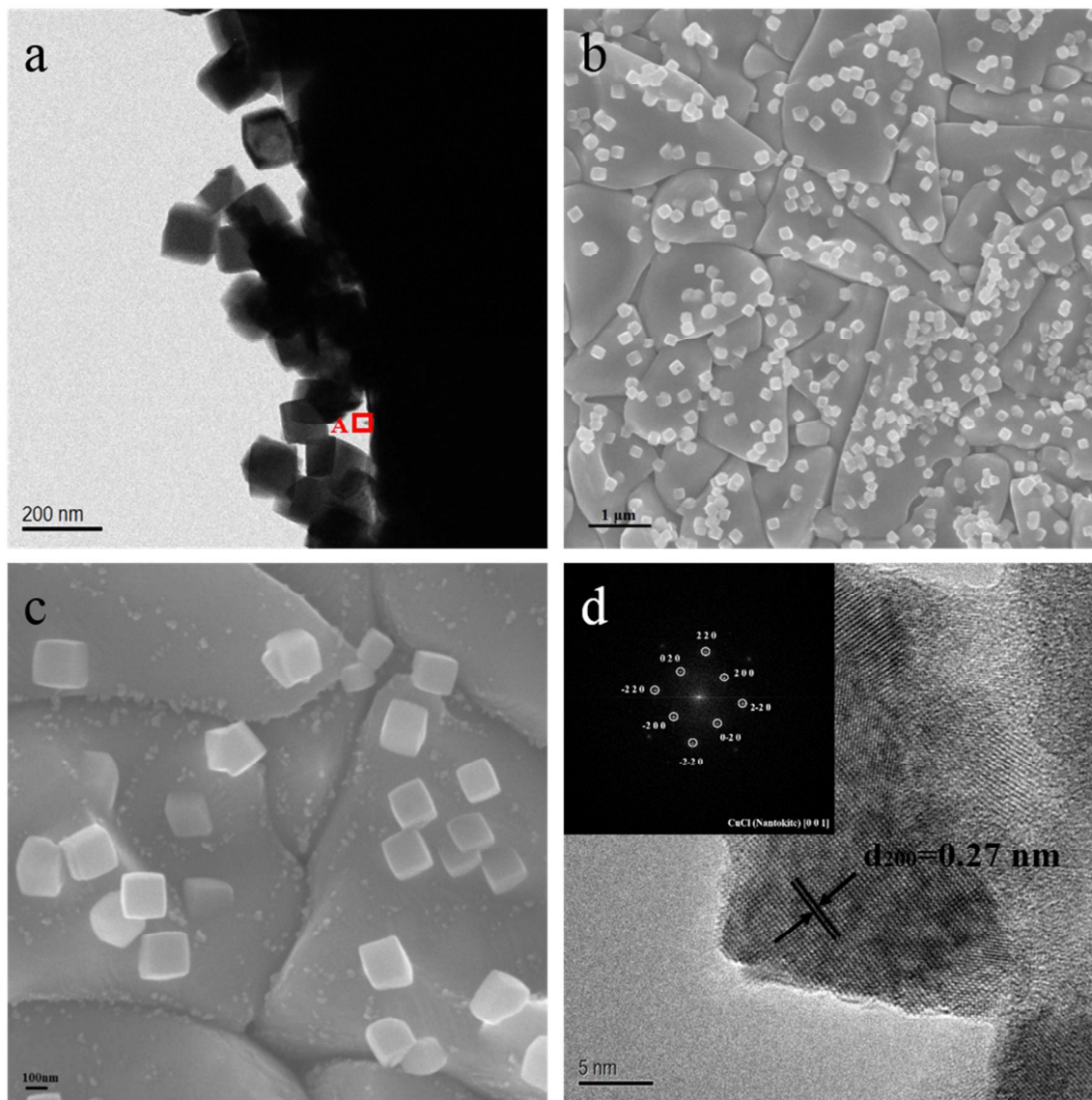


Figure 5. (a) A bright field TEM image of a copper needle after polarization to transpassive region in Figure 2; (b), (c) Low magnification and high magnification secondary electron SEM images of the same copper needle surface; (d) A HR-TEM image of the square region in Fig. 5 (a) and FFT pattern of taken from the small particle.

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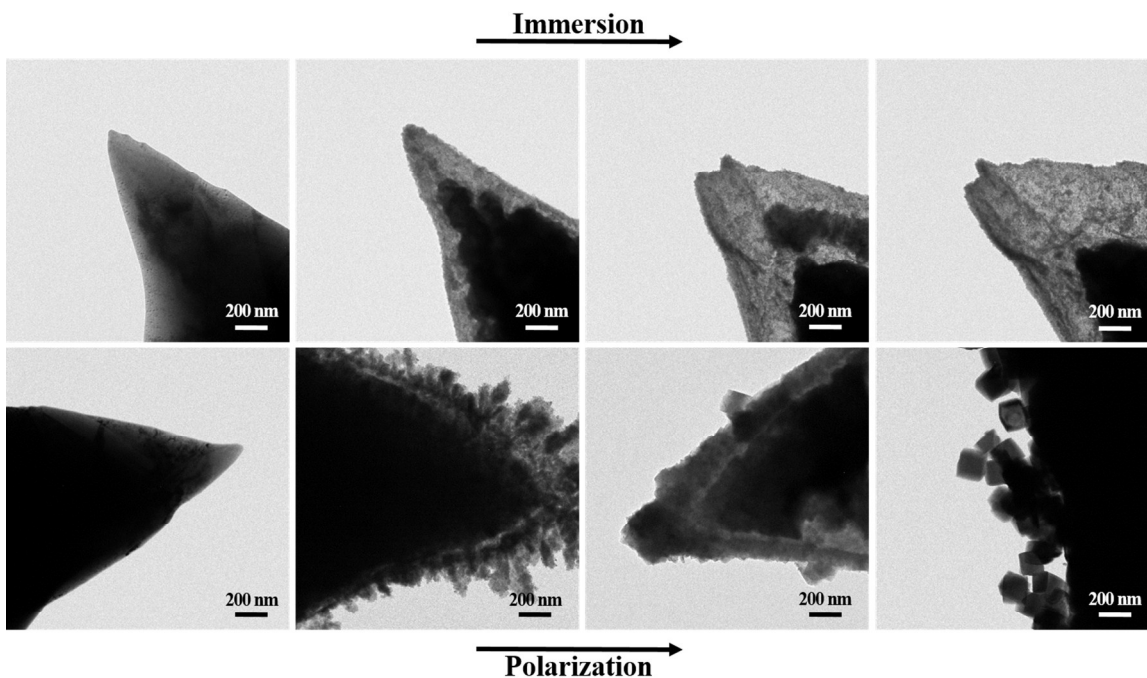
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Table of Contents (TOC) Image



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