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1 **Tailored copper oxidation in alkaline aqueous solution after**  
2 **helium cation implantation**

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4

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9 **Abstract**

10 Manipulating Cu oxidation is important for Cu anti-oxidation techniques  
11 and Cu oxide fabrication. In this study, Cu oxidation behavior after He<sup>+</sup>  
12 implantation was observed after exposure to 0.1 M aqueous NaOH, and the  
13 underlying microstructural evolution and mechanism were investigated.  
14 He<sup>+</sup> implantation and some C concomitantly introduced into the Cu surface  
15 accelerated formation of a thin oxide layer during the initial oxidation  
16 period, resulting in faster initial generation and more rapid growth of CuO  
17 during the subsequent oxidation. Furthermore, He<sup>+</sup> implantation  
18 homogenized the distribution of CuO on the Cu substrate. Our findings will  
19 increase researchers' understanding of the oxidation and corrosion behavior  
20 of Cu in aqueous alkaline conditions, and provide new insights into  
21 designing and growing Cu oxide nanostructures by ion implantation.

22

23 **Keywords:** helium ion implantation; copper oxidation; copper oxide  
24 nanostructure.

25 **Introduction**

26 As one of the most important metals, Cu is widely used in various  
27 industrial components (such as pipes and valves) as well as electrical  
28 systems and electronic devices; this wide use is due to its high thermal and  
29 electrical conductivities, ductility, and overall nontoxicity [1,2]. However,  
30 Cu readily oxidizes after several working cycles, even at room temperature;  
31 this oxidation impacts its performance in industrial and technological  
32 applications. Although many anti-oxidation techniques have been  
33 developed (such as alloying; electroplating; and surface-passivation  
34 technologies by using organic molecules, inorganic materials, or  
35 carbon-based materials as oxidation inhibitors [1,3]), applying these  
36 techniques has various drawbacks and limitations. For example, alloying  
37 with Cr or Ni degrades the thermal and electrical properties of Cu [4], and  
38 oxidation inhibitors often have limited success in large-scale applications  
39 [1,3]. However, two forms of Cu oxide [Cu(I) oxide ( $\text{Cu}_2\text{O}$ ) and Cu(II)  
40 oxide ( $\text{CuO}$ )] are excellent semiconductors that have a narrow band gap;  
41 and have drawn great interest in terms of their applications in catalytic, gas  
42 sensor, optoelectronic, and solar technologies. These Cu oxides can be

43 prepared by many methods (such as chemical and electrochemical  
44 deposition [5], anodization [6], and electrostatic spray deposition [7]).  
45 Furthermore, many methods have been exploited to design or fabricate  
46 specific copper oxides. For example, Ma et. al. [8] reported that an aligned  
47 two-dimensional single-crystal  $\text{Cu}_2\text{O}$  film can be deposited onto a Cu  
48 substrate by the polyol method. F-doped  $\text{SnO}_2$  glass [9],  $\text{TiO}_2$  nanotube  
49 arrays [10], and other materials have been used as substrates for growing  
50 Cu oxide nanostructures [11]. However, to date, the development of  
51 commercially viable copper oxides for photocatalysis, sensors, and  
52 solar-driven water-splitting remains challenging. Therefore, there is  
53 two-fold interest in Cu oxidation: mitigate Cu oxidation against  
54 technological failure, and exploit potential corresponding industrial  
55 applications; both lines of inquiry require manipulation of Cu oxidation.

56 It is generally accepted that oxidation and corrosion behavior  
57 corresponds to surface properties, which can be modified by surface  
58 treatment [2]. Ion implantation has been investigated to improve surface  
59 oxidation resistance by selectively implanting alloying elements. The  
60 nature of ion implantation facilitates introduction of any element into the

61 near-surface region of a solid in a controlled and reproducible manner [12],  
62 which is independent of most equilibrium constraints [13]. Ion implantation  
63 has been reported to improve the corrosion resistance of nickel [14] and  
64 stainless steel [15], aluminum alloy [16] and nickel–aluminum bronzes [17].  
65 Moreover, Zhao et al. [4] reported that a shallow implantation of Cr, Al,  
66 and Mg can enhance the oxidation resistance of Cu films and does not  
67 substantially affect the films' conductivity. C is usually introduced onto the  
68 surface concomitantly with the implanted ion due to the pump oil within  
69 the vacuum system [18,19]. In our recent studies of He<sup>+</sup> implantation on Cu  
70 [20], C was implanted into Cu to a depth of several nanometers  
71 concomitantly with He<sup>+</sup> ions; doing so passivated the Cu thermal oxidation  
72 by forming a barrier layer that blocked contact of Cu with air. An alkaline  
73 environment readily oxidizes or corrodes Cu, and has been widely  
74 investigated for anti-oxidation of Cu and Cu oxide growth [12,21-24].  
75 Because of the C-containing layer induced by He<sup>+</sup> implantation [20],  
76 He<sup>+</sup>-implanted Cu is also expected to impart passivation to oxidation in an  
77 alkaline environment. However, in this study, it is found that Cu implanted  
78 with He<sup>+</sup> exhibited enhanced CuO generation in alkaline aqueous solution,

79 rather than the expected passivation of oxidation. Furthermore,  
80 He<sup>+</sup>-implantation causes a relatively ordered configuration of CuO on the  
81 Cu substrate. The aim of this study was to clarify this oxidation behavior of  
82 Cu in alkaline aqueous solution after He<sup>+</sup> implantation. In this context, the  
83 morphology and microstructural evolution of Cu after oxidation was  
84 investigated by various microscopy techniques. A thin oxide layer rapidly  
85 formed on He<sup>+</sup>-implanted Cu after immersion in alkaline aqueous solution,  
86 subsequently resulting in faster initial generation and more rapid growth of  
87 CuO. These results will increase researchers' understanding of the  
88 oxidation and corrosion behavior of Cu in alkaline aqueous conditions, and  
89 provide new insights into designing and growing Cu oxide nanostructures.

90

## 91 **2. Materials and Methods**

### 92 2.1. Materials and ion implantation

93 Polycrystalline Cu (99.99%, size 10 mm × 10 mm × 1 mm) was  
94 purchased from Nilaco Corporation (Tokyo, Japan, No. 1054). NaOH was  
95 purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka,  
96 Japan, No. 19818863). The surface of Cu was polished with #2000 emery

97 paper, followed by mechanically polishing to a mirror plate with a buff  
98 grinder and 0.1 CR alumina as the polishing agent. Subsequently, each  
99 sample was mechanically polished for 10 min with a buff grinder and  
100 deionized water to remove any residual alumina. Finally, these samples  
101 were cleaned ultrasonically in acetone and deionized water sequentially 2×  
102 with each cleaning for 5 min, then rinsed with deionized water and dried in  
103 air.

104  $\text{He}^+$  implantation (100 keV) was performed on Cu substrates at room  
105 temperature to a fluence of  $5.0 \times 10^{15} \text{ cm}^{-2}$  with an ion flux of  $6.2 \times 10^{12} \text{ cm}^{-2}$   
106  $\text{ s}^{-1}$ . Raster scanning with an ion beam was carried out to achieve  
107 homogeneous implantation with a vacuum greater than  $1.0 \times 10^{-5} \text{ Pa}$  prior to  
108 implantation. After ion implantation, the  $\text{He}^+$ -implanted Cu was then  
109 cleaned with acetone and deionized water to remove the carbonaceous  
110 contamination that was absorbed onto the Cu surface during ion  
111 implantation [20]. The ion penetration profile of 100-keV  $\text{He}^+$  was also  
112 calculated with SRIM 2013 software, in which the full damage cascade  
113 model was used (Fig. S1).

114 2.2 Cu oxidation



115 Aqueous NaOH (0.1 M) was prepared. Bulk Cu samples (with or without  
116 He<sup>+</sup> implantation) were immersed in 0.1 M aqueous NaOH at room  
117 temperature for various times; then the oxidation state of these samples was  
118 detected and analyzed.

### 119 2.3 Characterization

120 An optical microscope (Nikon Eclipse LV150) was used to record the  
121 surface and morphology variation of the samples. Raman analysis was  
122 carried out with a Raman microscope (HORIBA XploRA), equipped with a  
123 532-nm-wavelength laser and a 2400-groove/nm grating. Raman spectra  
124 were obtained by confocal Raman microscopy with a confocal aperture of  
125 100  $\mu\text{m}$ . X-ray photoelectron spectroscopy (XPS) analysis (with a JEOL  
126 JPS-9200 spectroscope) was performed with a standard Al-K $\alpha$  X-ray  
127 source, a measured size of 1.0 mm in diameter, and a pressure maintained  
128 at  $10^{-7}$  Pa. Shirley-type background subtraction was performed before  
129 curve-fitting. XPS etching was used to analyze the sample composition in  
130 depth with 2-keV Ar<sup>+</sup> at an etching rate of about 2 nm/min, and an etching  
131 size of 3 mm  $\times$  3 mm.

132 The surface morphology of the sample was observed by field-emission

133 scanning electron microscopy (SEM; JEOL JSM-7001FA) at an  
134 accelerating voltage of 15 kV. A cross section of the bulk samples was  
135 made by using gallium ions in a focused-ion-beam (FIB) system (JEOL,  
136 JEM-90320FIB) at an accelerating voltage of 30 kV, which was then  
137 observed by SEM at a tilt angle of 70°. The transmission electron  
138 microscopy (TEM) samples were prepared by FIB at an accelerating  
139 voltage of 30 kV, and the samples were thinned to a final thickness of about  
140 100 nm. To minimize the damage introduced into the TEM samples by  
141 gallium ions with the FIB system, these TEM samples were then polished  
142 by using low-energy Ar<sup>+</sup> with GentleMill (TECHNOORG-IINDA Ltd. Co.,  
143 Gentle Mill IV8 HI). Both sides of the TEM samples were polished at 1 kV,  
144 at 15°, for 3 min; and 0.3 kV, at 10°, for 20 min. The microstructure was  
145 observed with a JEOL JEM-2000FX at 200 kV. By using Cs-corrected  
146 scanning transmission electron microscopy (STEM; FEI, Titan G2 60-300),  
147 the high-resolution (HR) TEM and high-angle annular dark field  
148 (HAADF)-STEM analyses were carried out at an operation voltage of 300  
149 kV.

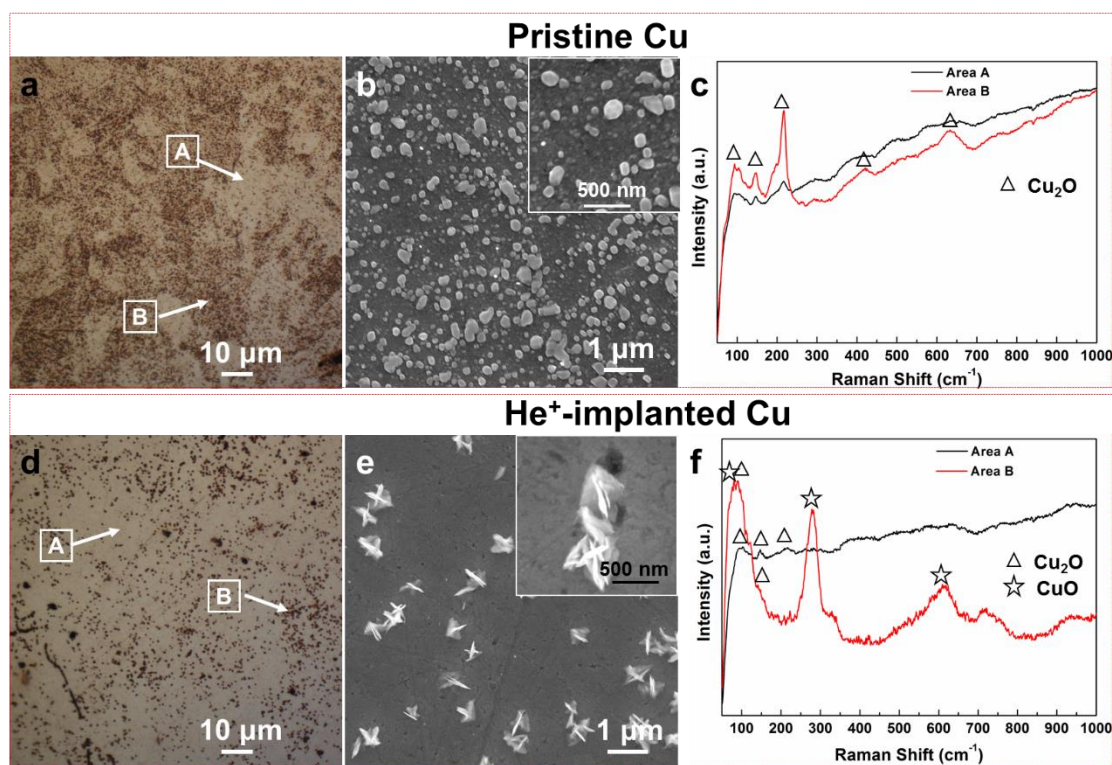
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### 151 **3. Results and discussion**

#### 152 3.1 Modified surface morphology evolution

153 Upon analysis by SEM, no obvious variation in the surface morphology  
154 was observed on the sample after He<sup>+</sup> implantation (Fig. S2). However,  
155 after immersion in 0.1 M NaOH for 5 h, distinct differences were found  
156 between pristine Cu and He<sup>+</sup>-implanted Cu, in terms of the surface  
157 morphology and oxidation products (Fig. 1). Regarding pristine Cu, some  
158 brown plaques were observed on the surface from the optical images [Fig.  
159 1(a)]; these plaques are attributable to the oxide islands [Fig. 1(b)]. These  
160 oxide islands were randomly distributed with a size ranging from several  
161 tens to hundreds of nanometers, resulting in a rough surface. By Raman  
162 microscopy [Fig. 1(c)], these island-like oxides were Cu<sub>2</sub>O; such findings  
163 are in good agreement with previous results that growth of Cu oxide  
164 proceeds through formation of oxide islands [2]. Regarding area A marked  
165 in the Fig. 1(a), where the surface color does not indicate a substantial  
166 change, the Raman spectrum of Cu<sub>2</sub>O was also detected at a relatively low  
167 intensity; suggesting that some smaller Cu<sub>2</sub>O islands formed, such as the  
168 small islands in the inset of Fig. 1(b). Regarding He<sup>+</sup>-implanted Cu, some

169 isolated dark dots were observed in the optical images [Fig. 1(d)]; they  
 170 were in the form of a leaf-like structure [refer to the SEM image in Fig.  
 171 1(e)]. The Raman results in Fig. 1(f) demonstrate that these leaf-like oxides  
 172 were CuO, rather than the Cu<sub>2</sub>O that formed on pristine Cu [Fig. 1(b)].  
 173 Furthermore, the Raman spectrum of area A marked in Fig. 1(d) (where no  
 174 CuO formed) indicates the characteristic peaks of Cu<sub>2</sub>O, suggesting that  
 175 Cu<sub>2</sub>O should also form on the Cu surface. However, in the SEM image of  
 176 Fig. 1(e), the surface of He<sup>+</sup>-implanted Cu was relatively smooth (except  
 177 the CuO), and there was no obvious island-like structure [Fig. 1(e)].



178  
 179 Fig. 1. (a, d) Optical images, (b, e) SEM images, and (c, f) Raman spectra of (a–c)

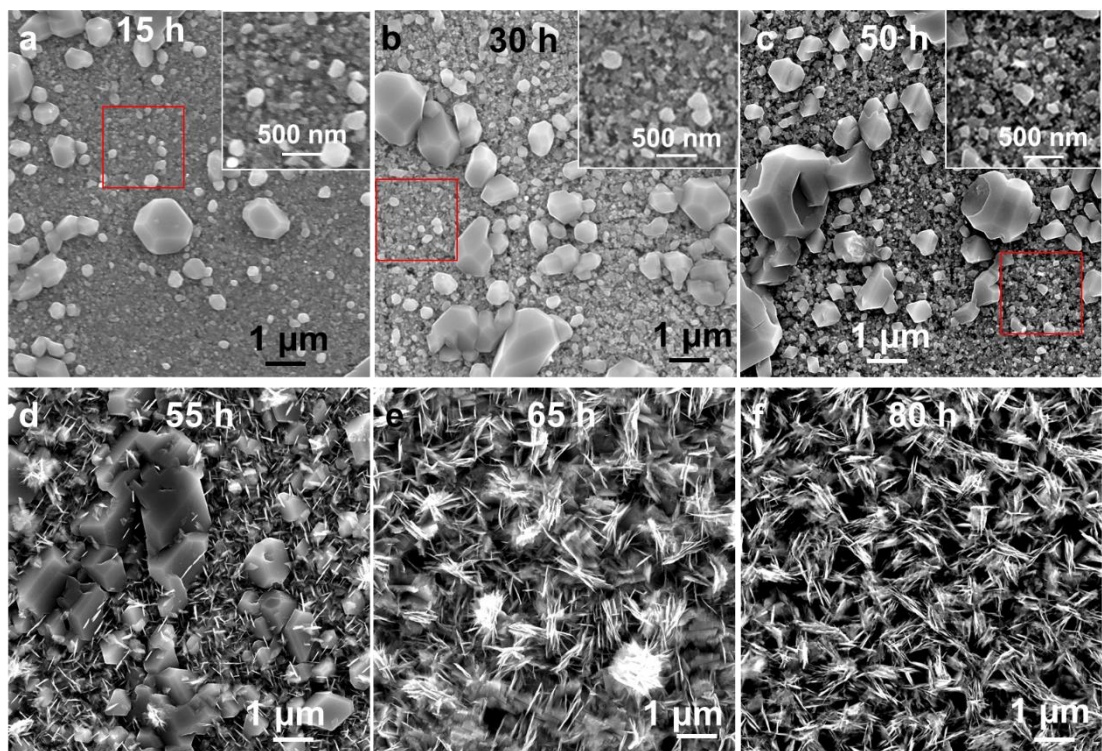
180 pristine Cu and (d–f) He<sup>+</sup>-implanted Cu in 0.1 M aqueous NaOH for 5 h. The insets in  
181 (b, d) are the SEM images at a higher magnification. The spectra in (c) and (f)  
182 correspond to the marked areas in (a) and (d), respectively.

183

184 Upon increasing the immersion time in aqueous NaOH, the evolution of  
185 the surface morphology and oxidation products of pristine Cu were  
186 analyzed by SEM (Fig. 2) and Raman microscopy (Fig. 3). In Figs. 2(a)–  
187 2(c), the Cu<sub>2</sub>O islands gradually increased in size via coalescence of oxide  
188 islands with increasing oxidation time. Up to 50 h, the oxidation products  
189 on pristine Cu were mainly Cu<sub>2</sub>O [Fig. 3(a)]. In addition, the areas without  
190 large Cu<sub>2</sub>O islands also became rougher with increasing oxidation time  
191 [Figs. 2(a)–2(c), insets]; these results are attributable to the formation and  
192 coalescence of smaller Cu<sub>2</sub>O islands, and corrosion (or dissolution) of the  
193 Cu surface [21]. After immersion in NaOH for 55 h, some small leaf-like  
194 oxides (size: about 200 nm) were evident on pristine Cu [Fig. 2(d)]; these  
195 oxides were identified as CuO by Raman microscopy [Fig. 3(b)]. The  
196 newly generated CuO gradually increased to a size of about 1 μm after  
197 immersion in 0.1 M NaOH for 65 h [Fig. 2(e)]. However, the size of these

198 leaf-like CuO structures remained about 1  $\mu\text{m}$  after immersion in NaOH for  
199 80 h [Fig. 2(f)], suggesting that the growth in size of the CuO decreased or  
200 even stopped after a certain duration of oxidation.

201 Regarding  $\text{He}^+$ -implanted Cu, compared with that in Fig. 1(e), more CuO  
202 nucleated on the Cu surface with increasing oxidation time up to 10 h [Figs.  
203 4(a) and 4(c)], with a size of about 500 nm. Over the subsequent 5 h, the  
204 CuO rapidly increased in size up to about 2  $\mu\text{m}$  [Figs. 4(b) and 4(c)]. The  
205 shape of CuO generated on pristine Cu and  $\text{He}^+$ -implanted Cu was similar.  
206 However, the CuO generated on  $\text{He}^+$ -implanted Cu exhibited a faster  
207 growth rate (in terms of the final size) than that on pristine Cu. Thus, it is  
208 clear that  $\text{He}^+$  implantation can modify the oxidation behavior of Cu in 0.1  
209 M NaOH, such as in terms of the faster initial generation and higher growth  
210 rate of CuO.

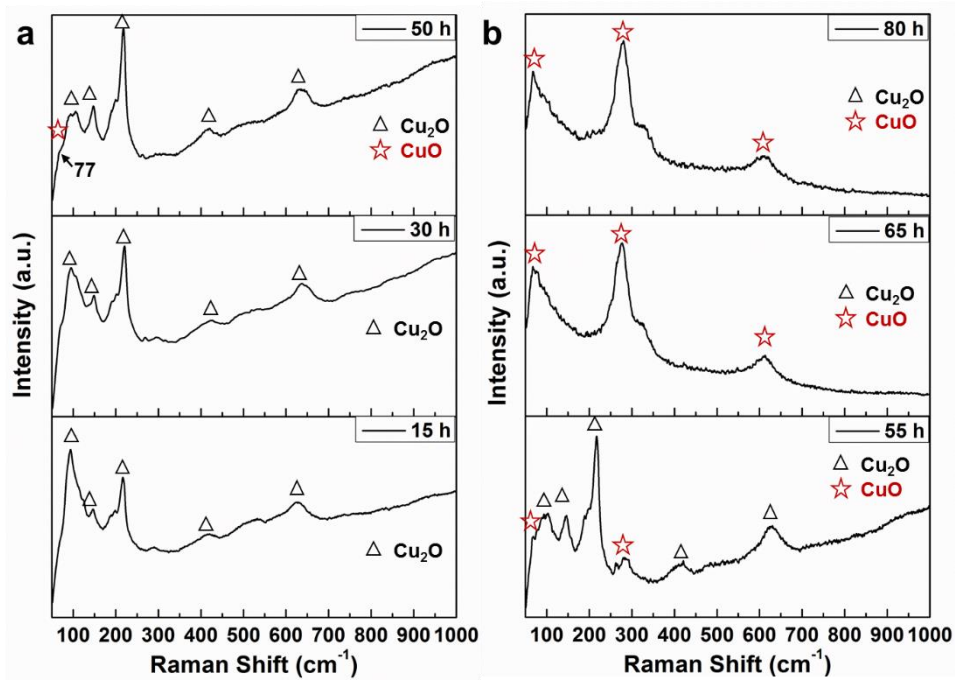


211

212 Fig. 2. SEM image of pristine Cu after immersion in 0.1 M aqueous NaOH for (a) 15 h,

213 (b) 30 h, (c) 50 h, (d) 55 h, (e) 65 h, and (f) 80 h. The insets in (a–c) are the enlarged

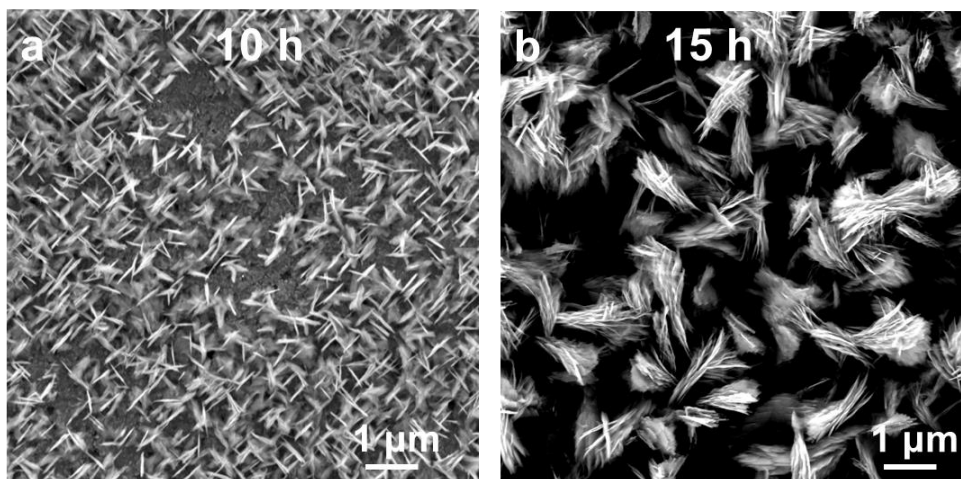
214 images of the marked areas in the corresponding images.



215

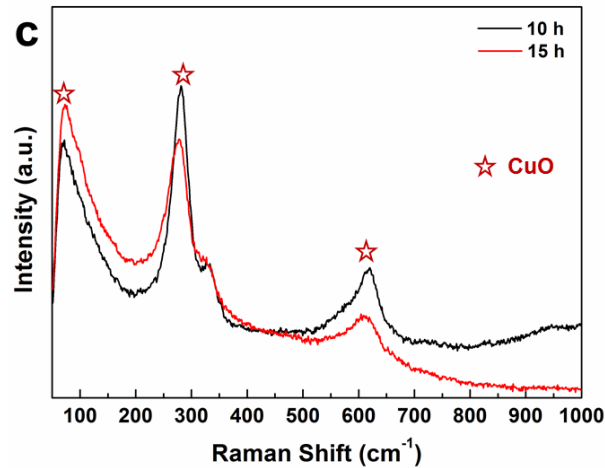
216 Fig. 3. Raman spectra of pristine Cu after immersion in 0.1 M aqueous NaOH for

217 various periods of time. (a) 15–50 h. (b) 55–80 h.



218





219

220 Fig. 4. SEM image of He<sup>+</sup>-implanted Cu after immersion in 0.1 M aqueous NaOH for

221 (a) 10 h and (b) 15 h, and (c) corresponding Raman spectra.

222

### 223 3.2 Fast initial generation of CuO on He<sup>+</sup>-implanted Cu

224 By an XPS-etch analysis, the C content profile in depth of the Cu with or

225 without He<sup>+</sup> implantation was detected in this study. A higher content and

226 deeper distribution of C was observed in He<sup>+</sup>-implanted Cu than that in

227 pristine Cu [Fig. 5(a)], indicating that additional C was introduced into this

228 sample to a depth of about 6 nm during He<sup>+</sup> implantation. A small quantity

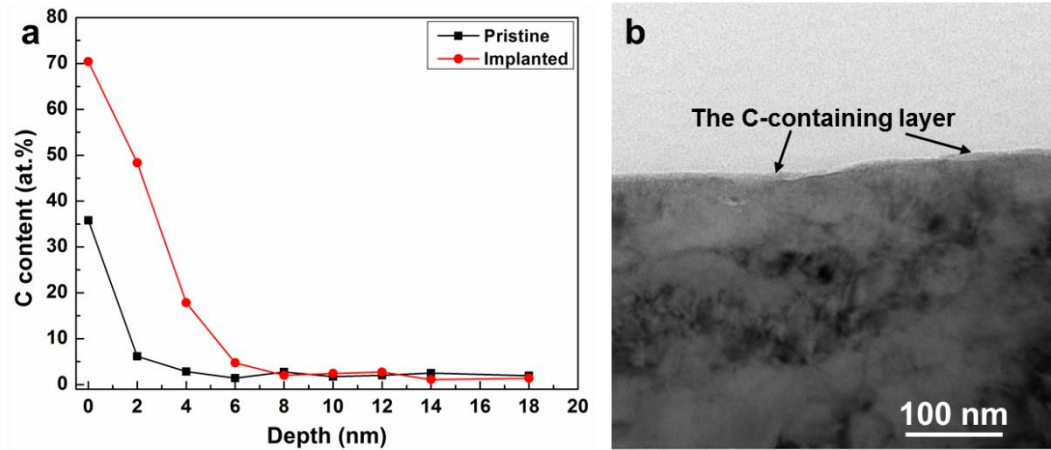
229 of C was also detected on the surface of pristine Cu, which is attributable to

230 the dust in the air that was absorbed onto the Cu surface, which was usually

231 detected by XPS analysis. By TEM, a film was observed that covered the

232 surface of He<sup>+</sup>-implanted Cu [Fig. 5(b)]; which should correspond to the

233 C-containing barrier layer [20].

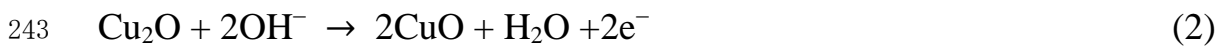
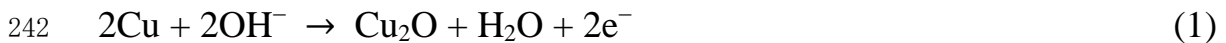


234

235 Fig. 5. (a) C content profile in depth detected by X-ray photoelectron spectroscopy  
236 etching for the samples with and without He<sup>+</sup> implantation. (b) Cross-sectional  
237 transmission electron microscopy image of He<sup>+</sup>-implanted Cu with a fluence of 5×10<sup>15</sup>  
238 cm<sup>-2</sup>.

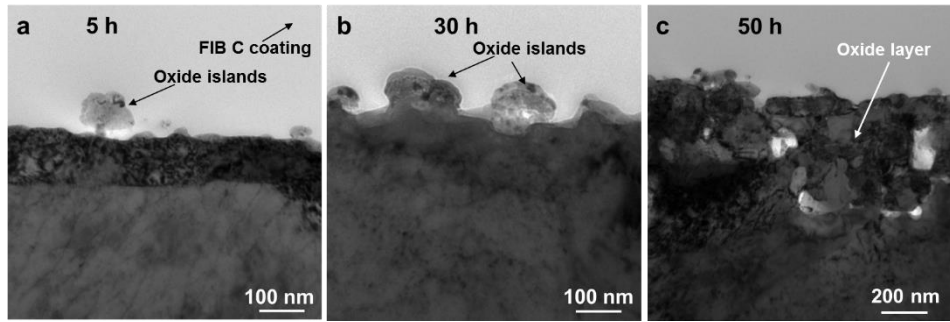
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240 In alkaline solution, the formation of Cu oxide is a two-step growth  
241 process and can be described as follows [23,24]:



244 Furthermore, generation of CuO usually occurs after formation of a  
245 continuous Cu<sub>2</sub>O film on the Cu substrate [21,24]. By TEM, the evolution  
246 of the surface morphology on pristine Cu was observed (Fig. 6). For

247 pristine Cu in 0.1 M NaOH for 5 h [Fig. 6(a)], the oxidation state along the  
248 Cu surface was inhomogeneous, with some areas covered with Cu<sub>2</sub>O  
249 islands and some areas not covered. After immersion in NaOH for 30 h,  
250 islands on the Cu surface enlarged via coalescence of the islands, but there  
251 were still some areas that were not covered by Cu<sub>2</sub>O islands [Fig. 6(b)]. By  
252 increasing the oxidation time to 50 h, a continuous Cu<sub>2</sub>O film was observed  
253 on the Cu [Fig. 6(c)]. Over the 5 h after formation of this Cu<sub>2</sub>O film,  
254 leaf-like CuO was evident [Fig. 2(d)]. These results agree well with  
255 previous reports that the generation of CuO usually occurs after formation  
256 of a continuous Cu<sub>2</sub>O film [24]. Meanwhile, although the whole surface of  
257 pristine Cu is covered by the Cu<sub>2</sub>O film after immersion in NaOH for 55h,  
258 the nucleation of CuO is not homogeneous as show in the Fig. 2(d). More  
259 CuO preferentially nucleated at the area with a thin oxide film (i.e. without  
260 large Cu<sub>2</sub>O island) [Fig. 2(d)], which suggests that a thinner oxide film  
261 could accelerate the generation of CuO.



262

263 Fig. 6. Cross-sectional bright-field TEM image of pristine Cu after immersion in 0.1  
 264 NaOH for (a) 5 h, (b) 30 h, and (c) 50 h.

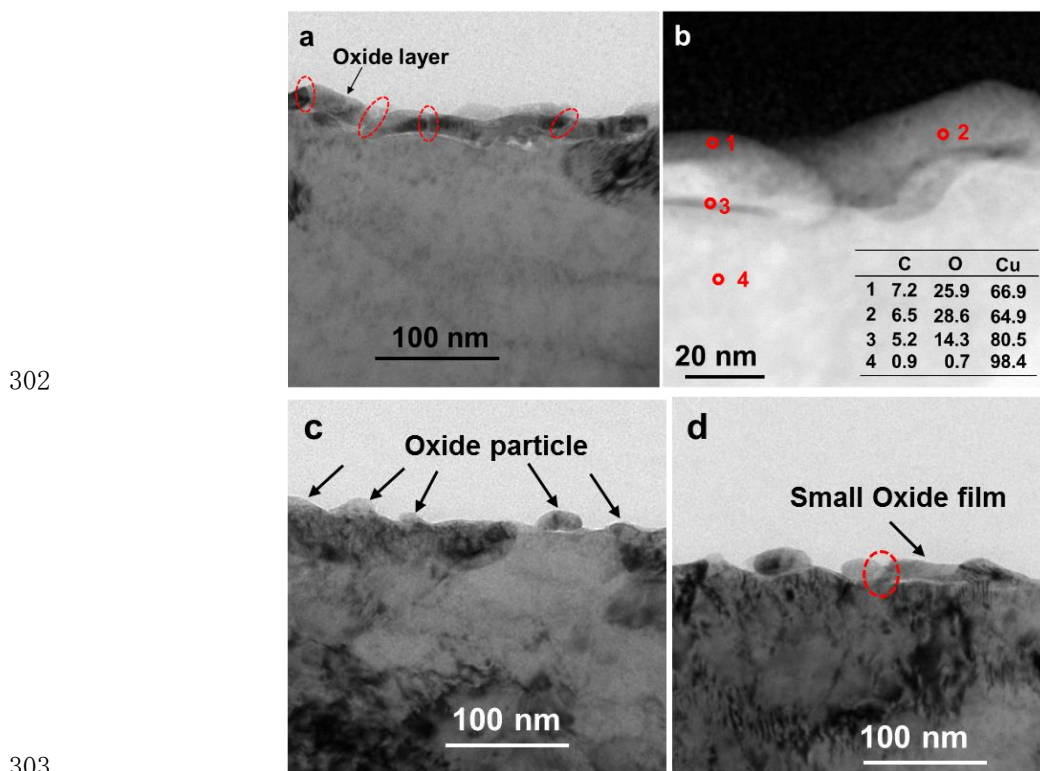
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266 Regarding  $\text{He}^+$ -implanted Cu after immersion in 0.1 NaOH for 5 h, a  
 267 film was observed on the Cu surface in the bright-field TEM images [Fig.  
 268 7(a)], with a thickness of about 20 nm. In accordance with observations by  
 269 HAADF-STEM in Fig. 7(b), this film exhibited a comparatively weaker  
 270 bright contrast than that of the Cu substrate. HAADF-STEM images are  
 271 sensitive to the atomic number ( $z$ ) of the sample; i.e., heavier-element  
 272 atoms exhibit a brighter contrast. Thus, this layer structure should have a  
 273 lower atomic mass than that of Cu [25]. In accordance with detection by  
 274 STEM-EDS, the O/Cu atomic ratio in areas 1 and 2 was close to that of  
 275  $\text{Cu}_2\text{O}$ . By also considering the Raman results in Fig. 1(f),  $\text{Cu}_2\text{O}$  formed on  
 276 the Cu surface; i.e.,  $\text{Cu}_2\text{O}$  was present in this film. These results indicate  
 277 that to some extent a  $\text{Cu}_2\text{O}$  film already formed on  $\text{He}^+$ -implanted Cu after

278 immersion in 0.1 M aqueous NaOH for 5 h. Considering that a  $\text{Cu}_2\text{O}$  film  
279 usually must form before generation of CuO, and that CuO preferentially  
280 nucleate at the area with a thinner oxide film [Fig. 2(d)], the rapidly formed  
281  $\text{Cu}_2\text{O}$  thin film should account for the faster initial generation of CuO on  
282  $\text{He}^+$ -implanted Cu [Fig. 1(e)].

283 The boundary between different oxide particles was observed in this  
284 oxide film [Figs. 7(a) and 7(b), such as the area marked by a red circle in  
285 Fig. 7(a)], suggesting that this film also formed through coalescence of  
286 oxide particles. To better understand the evolution of oxide in  
287  $\text{He}^+$ -implanted Cu, an oxidation experiment over a briefer period of time  
288 was carried out for this sample [Figs. 7(c) and 7(d)]. Some small oxide  
289 particles (about 15 nm in thickness) were observed on  $\text{He}^+$ -implanted Cu  
290 after immersion in 0.1 M NaOH for 2 h [Fig. 7(c)], which gradually grew  
291 into a small oxide film with increasing oxidation time to 3 h [Fig. 7(d)].  
292 This result confirms the following: the oxide film that formed on  
293  $\text{He}^+$ -implanted Cu proceeded through coalescence of oxide particles.  
294 Compared with that of the oxide islands on pristine Cu [Fig. 6(a)], the  
295 thickness of this oxide film on  $\text{He}^+$ -implanted Cu [Fig. 7(a)] was thinner,

296 suggesting that lengthways growth of oxide on He<sup>+</sup>-implanted Cu was  
 297 limited. Furthermore, the evolution of oxide on He<sup>+</sup>-implanted Cu [Figs.  
 298 7(a), 7(c), and 7(d)] implies a rapid lateral growth of oxide through  
 299 coalescence of oxide particles. Thus, the rapid formation of a thin oxide  
 300 film on He<sup>+</sup>-implanted Cu is attributable to the limited lengthways growth  
 301 and enhanced lateral growth of the oxide.



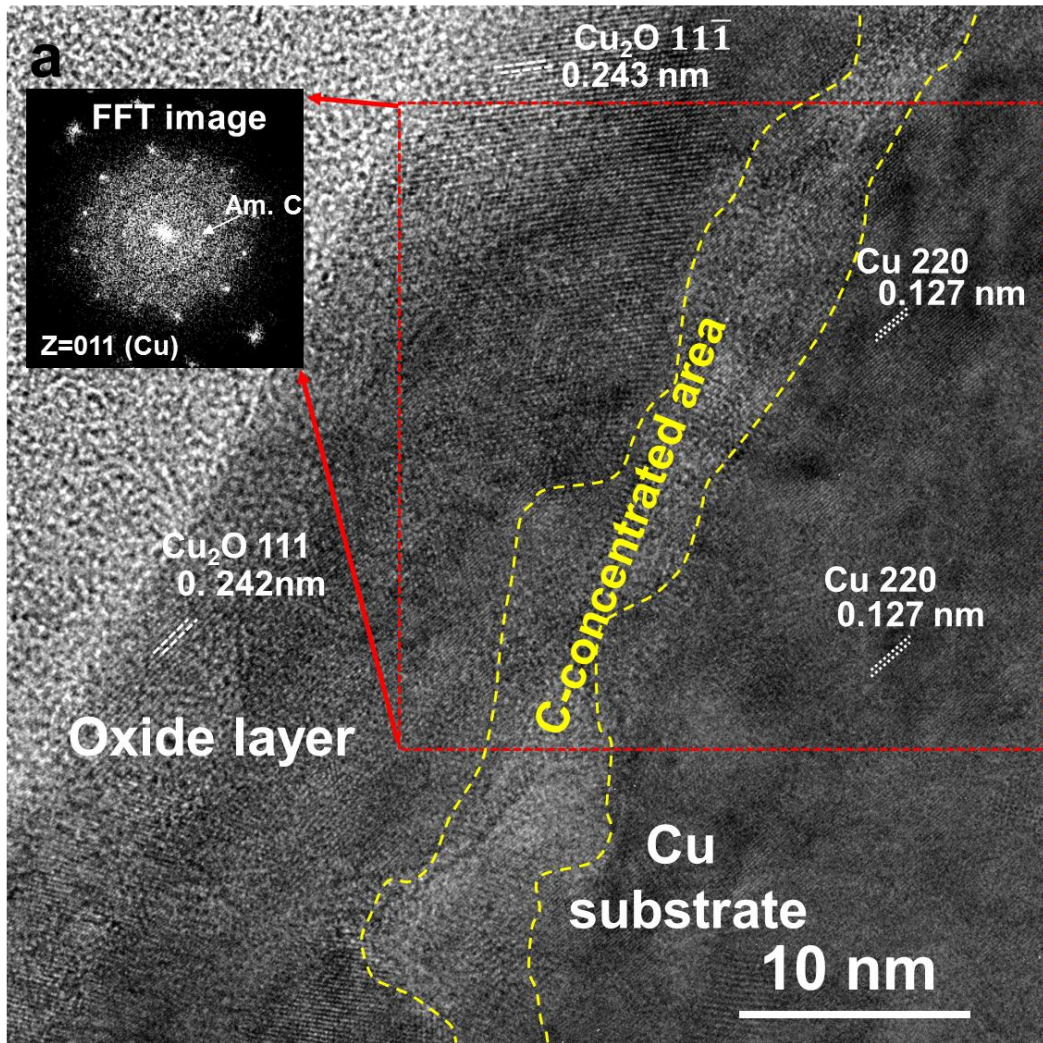
304 Fig. 7. (a) Cross-sectional bright-field TEM image and (b) HAADF-STEM image of  
 305 He<sup>+</sup>-implanted Cu after immersion in 0.1 M NaOH for 5 h. The table inset in (b) is the  
 306 STEM-EDS results of the corresponding area. (c and d) Cross-sectional bright-field  
 307 TEM image of He<sup>+</sup>-implanted Cu after immersion in 0.1 M NaOH for (c) 2 h and (d) 3

308 h.

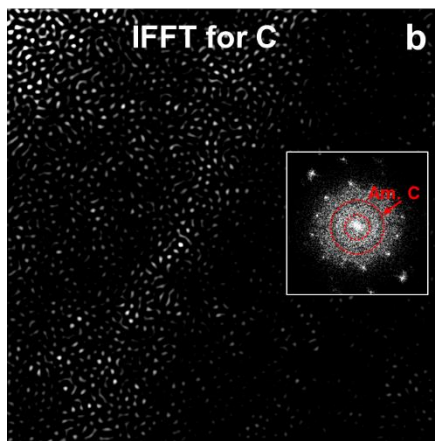
309 To better understand the formation of this oxide film on He<sup>+</sup>-implanted  
310 Cu, the microstructure of this film was analyzed by HR-TEM. In Fig. 8(a),  
311 the fast-Fourier transform (FFT) of a selected area around the oxide film  
312 and Cu substrate indicated a ring pattern of amorphous C (Am. C). By the  
313 inverse fast-Fourier transform (IFFT) technique, there was C in this oxide  
314 film [Fig. 8(b)]; with some C concentrated at the upper surface of the oxide  
315 film, and the interface between the oxide film and Cu substrate [marked by  
316 the dashed yellow line in the Fig. 8(a)]. These results agree well with the C  
317 content profile in depth detected by XPS-etching techniques [Fig. 8(c)].  
318 Because no additional C entered the sample during oxidation, the C in the  
319 oxide film is attributable to the C introduced during He<sup>+</sup> implantation (Fig.  
320 5). For a comparison, Fig. 8(d) shows a HR-TEM image of Cu<sub>2</sub>O islands  
321 on pristine Cu after immersion in NaOH for 5 h. There was no  
322 C-concentrated layer around the interface between the Cu oxide and Cu  
323 substrate. Oxidation of Cu in an aqueous environment implies electronic  
324 exchanges (electrochemical reactions) and ionic species transport between  
325 the base metal and environment, and it has been demonstrated that the

326 presence of C passivated Cu oxidation [20, 26]. In the present study, C was  
327 concentrated at the upper surface of the oxide film (and the interface  
328 between the oxide film and Cu substrate) on He<sup>+</sup>-implanted Cu after  
329 immersion in NaOH for 5 h. Thus, the limited the lengthways growth of the  
330 oxide in He<sup>+</sup>-implanted Cu should be mainly attributed to the C (introduced  
331 during He<sup>+</sup> implantation). Furthermore, Cu oxide more-readily nucleates  
332 and increases in size at regions with surface defects [2,12]. These processes  
333 might facilitate establishment of an oxide film; accelerated formation of an  
334 oxide film was observed on Ar<sup>+</sup>-implanted Cu due to surface defects  
335 induced by ion implantation [20]. In this study, because of ion sputtering,  
336 surface defects are also expected to be introduced by He<sup>+</sup> implantation. By  
337 a comparison of Figs. 6(a) and 7(c), more oxide nuclei formed on  
338 He<sup>+</sup>-implanted Cu than on pristine Cu over the initial oxidation period  
339 because of surface defects; resulting in enhanced lateral growth of Cu oxide  
340 via coalescence of Cu oxide particles and rapid formation of an oxide film.

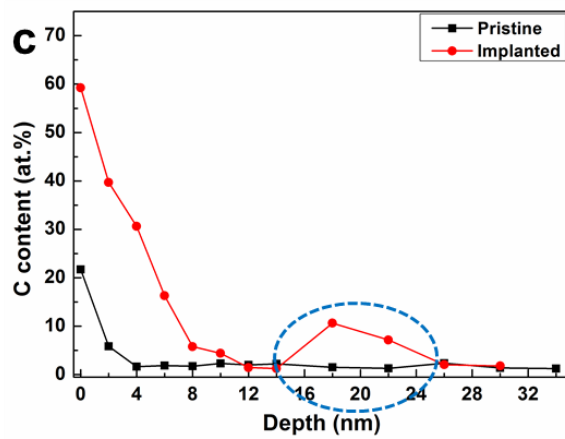


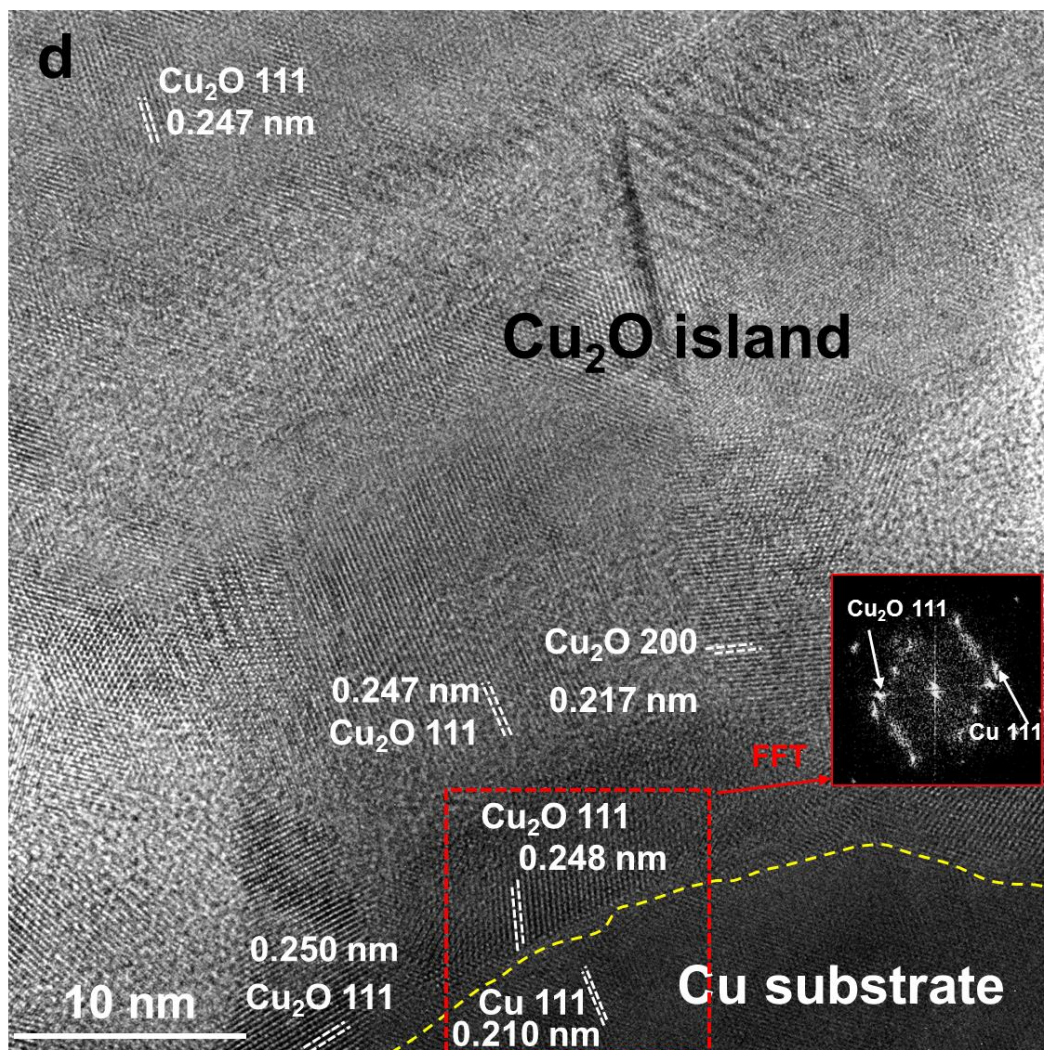


341



342





343

344 Fig. 8. (a) HR-TEM image of an oxide layer on  $\text{He}^+$ -implanted Cu. The inset is a FFT

345 image of the selected area marked by a red square. (b) IFFT for C of the selected area in

346 (a). (c) C content profile in depth detected by XPS etching; corresponding spectra

347 provided in Fig. S3. (d) HR-TEM image of  $\text{Cu}_2\text{O}$  islands on pristine Cu after immersion

348 in 0.1 M NaOH for 5 h.

349

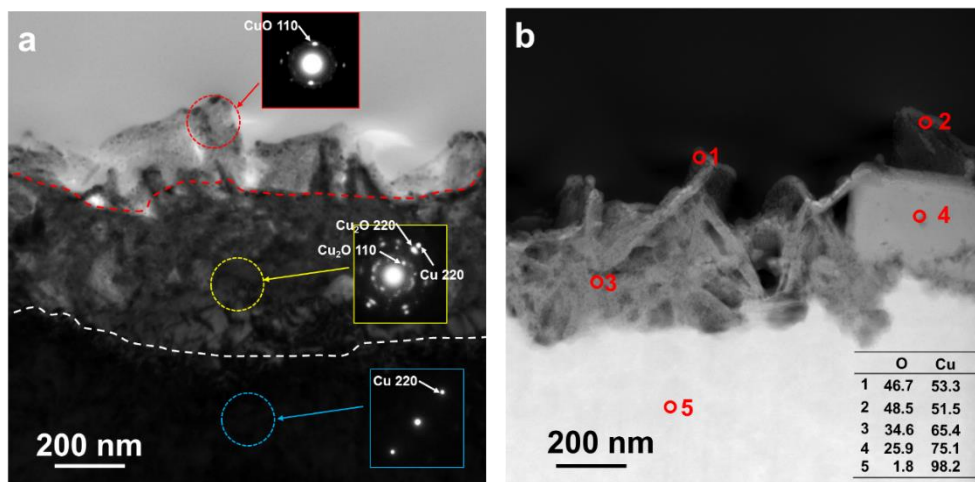
350 3.3 Rapid growth of CuO on  $\text{He}^+$ -implanted Cu

351 After formation of a  $\text{Cu}_2\text{O}$  layer, leaf-like  $\text{CuO}$  was generated on both  
352 pristine  $\text{Cu}$  [55 h; Fig. 2(d)] and  $\text{He}^+$ -implanted  $\text{Cu}$  (5 h; Fig. 1(d)). The  
353 configuration of  $\text{CuO}$  on the surface was observed by TEM and HAADT-  
354 STEM (Fig. 9, pristine  $\text{Cu}$ ; and Fig. 10,  $\text{He}^+$ -implanted  $\text{Cu}$ ). In Fig. 9(a),  
355 three layers were distinguished by image contrast and selected-area  
356 electron diffraction: i.e., the top  $\text{CuO}$  layer, middle  $\text{Cu}_2\text{O}$  layer, and bottom  
357  $\text{Cu}$  substrate; confirmed by STEM-EDS [Fig. 9(b)]. The thickness of the  
358  $\text{Cu}_2\text{O}$  layer in pristine  $\text{Cu}$  was about 300 nm [Fig. 10(a)]. However, in  
359  $\text{He}^+$ -implanted  $\text{Cu}$ , there was no obvious  $\text{Cu}_2\text{O}$  layer by relatively  
360 low-magnification TEM and selected-area electron diffraction [Fig. 10(a)].  
361 By STEM-EDS, the composition of various areas was detected [Fig.  
362 10(b)]; the area around the boundary of  $\text{Cu}$  and  $\text{CuO}$  [black square in Fig.  
363 10(b)] was analyzed by HR-TEM. A thin  $\text{Cu}_2\text{O}$  layer with a thickness of  
364 about 4 nm formed between the  $\text{Cu}$  and  $\text{CuO}$ , which was substantially  
365 thinner than that on pristine  $\text{Cu}$  [about 300 nm in Fig. 9(a)].

366 In Figs. 9 and 10, double oxide layers were confirmed on both pristine  
367  $\text{Cu}$  and  $\text{He}^+$ -implanted  $\text{Cu}$ , with an outer layer of leaf-like  $\text{CuO}$  and an  
368 inner layer of  $\text{Cu}_2\text{O}$ . However, the  $\text{Cu}_2\text{O}$  layer that formed on

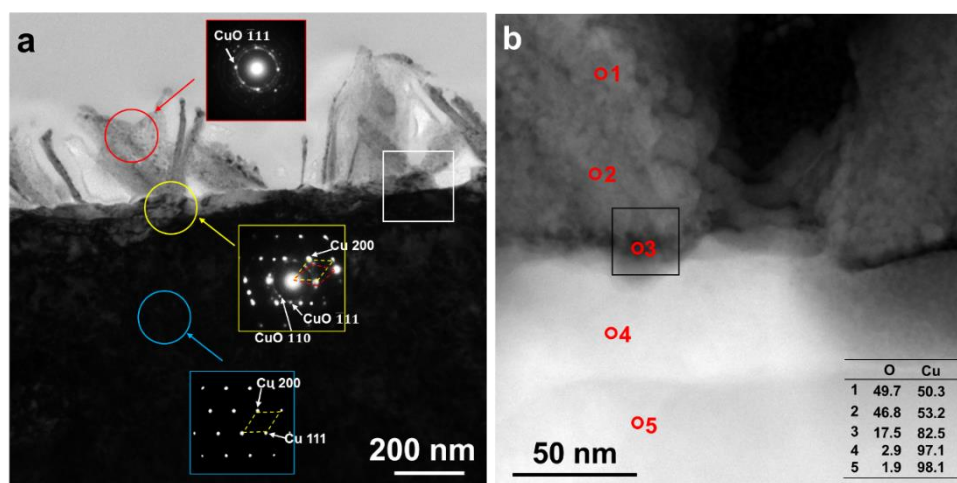
369 He<sup>+</sup>-implanted Cu was much thinner than that on pristine Cu. Oxidation of  
370 Cu in an aqueous environment proceeds with ionic species transport  
371 between the base metal and environment. A dense Cu<sub>2</sub>O layer can hinder  
372 growth of CuO by blocking ionic species transport between the Cu and  
373 solution [21,22,24]. Therefore, the more-rapid growth of CuO on  
374 He<sup>+</sup>-implanted Cu (Fig. 4) than that on pristine Cu [Figs. 2(d)–2(f)] is  
375 mainly attributable to the thinner Cu<sub>2</sub>O layer on the former. In addition, the  
376 lower number density of CuO [Figs. 4(b) and 2(f)] might also contribute to  
377 the higher growth rate of CuO on He<sup>+</sup>-implanted Cu compared with that on  
378 pristine Cu.

379 The growth of CuO slowed after immersion in 0.1 M NaOH for 65 h  
380 [Figs. 2(e) and 2(f)], which was also observed in anodization synthesis of  
381 CuO [24]. By comparing the Cu<sub>2</sub>O layer in Figs. 5(c) and 9(a), the porous  
382 Cu<sub>2</sub>O layer became more compact with increasing oxidation time [Fig.  
383 9(a)]. The denser Cu<sub>2</sub>O layer can block direct contact of the Cu substrate  
384 with the solution, and decrease the transport of ionic species between them  
385 [21]; resulting in a decreased growth rate of CuO on pristine Cu.

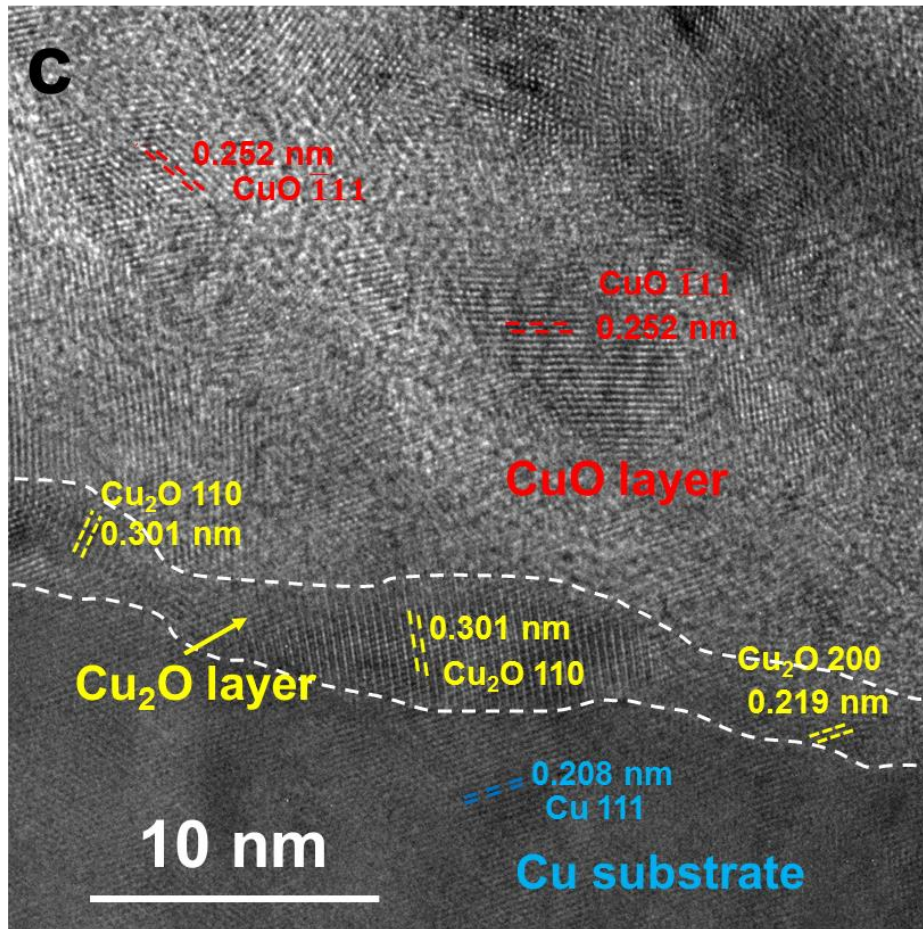


386

387 Fig. 9. (a) Cross-sectional bright-field TEM image and (b) HAADF-STEM image of  
 388 pristine Cu after immersion in NaOH for 55 h. The table inset in (b) shows the STEM-  
 389 EDS results of the corresponding area.



390



391

392 Fig. 10. (a) Cross-section bright-field TEM image and HAADF-STEM image of

393 He<sup>+</sup>-implanted Cu after immersion in NaOH for 10 h. The table inset in (b) is the

394 STEM-EDS results of the corresponding area. (c) HR-TEM image around the Cu/CuO

395 interface.

396

### 397 3.4 Potential applications of ion implantation in the Cu oxidation

398 In our previous studies, the C-containing barrier layer that formed on

399 He<sup>+</sup>-implanted Cu passivated Cu thermal oxidation [20]. However, in this

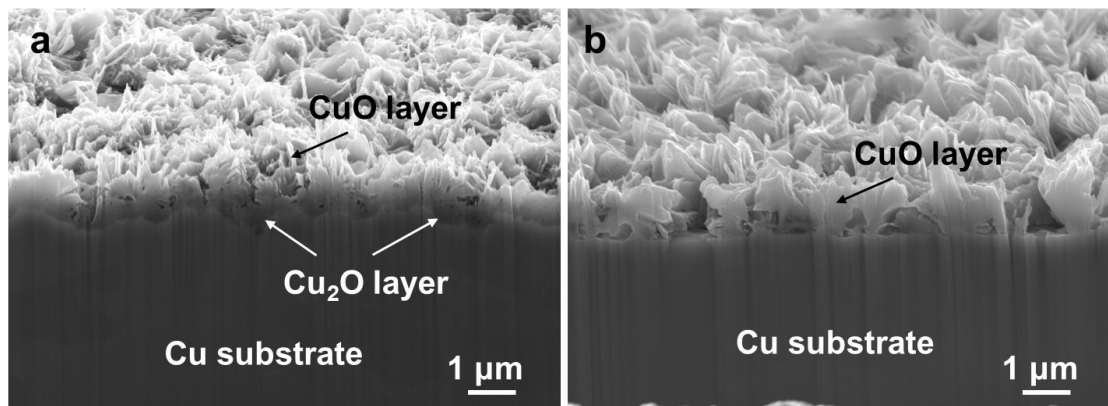
400 study, the C (introduced during He<sup>+</sup> implantation) accelerated generation  
401 and growth of CuO on He<sup>+</sup>-implanted Cu; resulting in a heavier oxidation  
402 state on He<sup>+</sup>-implanted Cu than that on pristine Cu in alkaline aqueous  
403 solution. However, during the initial oxidation period (in NaOH for 5 h),  
404 the C-containing layer limited the lengthways growth of oxide on  
405 He<sup>+</sup>-implanted Cu [Fig. 7(a)]; which implies that a thicker C-containing  
406 layer might result in a stronger passivation effect on Cu oxidation.  
407 Furthermore, the modified Cu oxidation induced by He<sup>+</sup> implantation also  
408 suggests that ion implantation might be useful to modify CuO growth.

409 CuO is an important semiconductor that is used in photoelectronic,  
410 catalytic, and solar energy technologies [2,27]. Various studies have been  
411 performed to exploit and develop appropriate methods for Cu oxide  
412 nanostructure growth [28,29]; such as increasing the efficiency by  
413 decreasing the fabrication time [22], preparing highly ordered arrays of Cu  
414 oxide nanostructures [8,24], and low-cost fabrication by photosynthesis  
415 [29]. However, to date, developing commercially viable copper oxides used  
416 for photocatalytic and sensor applications remains challenging. In this  
417 study, a faster initial generation and more-rapid growth of CuO was

418 achieved by implanting some C into the Cu surface by He<sup>+</sup> implantation;  
419 which suggests that ion implantation, such as C<sup>+</sup> implantation, might be  
420 used to decrease the time or energy cost for fabricating CuO. Furthermore,  
421 regarding pristine Cu, a rough and loose surface was formed before  
422 generating CuO [Fig. 2(c)]; resulting in a disordered distribution of CuO on  
423 the Cu substrate [Figs. 2(f) and 11(a)]. However, regarding He<sup>+</sup>-implanted  
424 Cu, the surface of the Cu substrate after forming CuO was still relatively  
425 smooth [Figs. 10(a) and 11(b)]; corresponding to a relatively uniform and  
426 ordered distribution of CuO. This indicates that the configuration of CuO  
427 on the Cu support was modified by ion implantation. Overall, both the  
428 more-rapid growth of CuO and the ordered distribution of CuO induced by  
429 He<sup>+</sup> implantation suggests that shallow ion implantation, such as that by  
430 He<sup>+</sup> or C<sup>+</sup>, can be used to modulate CuO growth. In addition, the modified  
431 configuration by He<sup>+</sup> implantation may lead to some revisions of optical or  
432 electrical properties of CuO film. The difference between the pristine  
433 sample and He<sup>+</sup>-implanted sample in term of the bonding strength of CuO  
434 film and substrate and optical absorption property of CuO is shown in the  
435 supplementary. More investigations about the revised properties of CuO



436 will be performed in the future.



437

438 Fig. 11. Cross-sectional SEM image, viewed at a tilt angle of 70°. (a) Pristine Cu after  
439 immersion in 0.1 M NaOH for 80 h. (b) He<sup>+</sup>-implanted Cu after immersion in 0.1 M  
440 NaOH for 15 h.

441

## 442 5. Conclusions

443 The oxidation behavior of He<sup>+</sup>-implanted Cu in 0.1 M aqueous NaOH  
444 was investigated. Because of He<sup>+</sup> implantation, and the C that was  
445 concomitantly implanted into the Cu surface (which originated from the  
446 pump oil within the vacuum system), accelerated oxidation was observed in  
447 reference to the faster initial generation and more-rapid growth of CuO.  
448 Furthermore, He<sup>+</sup> implantation rendered the distribution of the CuO on the  
449 Cu substrate relatively uniform and ordered. The more-rapid growth and  
450 uniform distribution of CuO induced by He<sup>+</sup> implantation suggests that ion

451 implantation can be used to modulate the fabrication of CuO  
452 nanostructures.

453

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