Supplementary Information

One-step transformation of Cu to Cu$_2$O in alkaline solution

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1. Experimental details

1.1 Materials

NaOH (DaeJung Chemical, > 97.0%), Cu(NO₃)₂ 2.5H₂O (Aldrich, 99.99+%), lactic acid (Kanto, 85.0~92.0% solution in water), Ethanol (Aldrich, 95%) were used without further purification. Cu foils (Aldrich, thickness 0.5 mm, 99.98%) were cut to small pieces with the size of 2 cm × 2 cm were cleaned with the order of ethanol, deionized water and ethanol in sonication bath (Hwashin, Powersonic 410) each for 5 min and quickly dried in N₂ flow for using. The commercial fluorine-doped tin oxide (FTO) (Pilkington FTO glass (TEC 8), 6~9 ohm/sq) glass (2 cm × 3 cm ) were cleaned with ethanol, acetone, deionized water in sonication bath each for 10 min and quickly dried in N₂ flow before using. All chemicals were used without further purification.

1.2 Electrodeposition of Cu film on FTO glass (Cu/FTO)

Cu film was deposited on FTO glass as the similar process as our previous report.[1] Cu was electrodeposited in a conventional three-electrode cell system using a potentiostat PL-9. FTO glass was used as the working electrode. The FTO glass was dipped into the electrolyte solution and the immersed area was 4 cm². A coiled platinum wire and an Ag/AgCl in 3 M KCl electrode were used as counter and reference electrode, respectively. Cu films were deposited from the aqueous solution containing 0.1 M Cu(NO₃)₂ and 3 M lactic acid with pH 5 at -0.4 V vs. Ag/AgCl for 10 min without stirring under ambient at 24 °C. The pH was adjusted by adding 4 M NaOH.

1.3 Synthesis of Cu₂O/Cu and Cu₂O/FTO films

a. Cu₂O/Cu₁

Cu₁ foil was put into the glass bottle (volume: 100 ml) containing a solution of 20 ml 4 M NaOH; then the bottle was sealed by a cap and heated on a hot plate to 80 °C. After heating around 1 h, the bottle was taken away and keeping at room temperature for 4 days.

b. Cu₂O/Cu₂

In a typical procedure, the sealed glass bottle (volume: 100 ml) containing a solution of 20 ml 4 M NaOH heated on a hot plate to 80 °C around 1 h; then the bottle was taken away from the hot plate and...
put the Cu$_2$ into the solution vertically and sealed again followed by keeping at room temperature for 14 h.

For comparison, the same experimental processes were also applied at different concentrations of NaOH (2 M, 6 M and 8 M). The morphology dependent on reaction time was carried out in 2 M NaOH solution with different times of 28 h, 60 h and 20.5 days. In addition, the similar immersion processes were directly carried out at room temperature (24 °C); Cu$_2$ foils (2 cm × 2 cm) were vertically kept in 20 mL NaOH aqueous solution with different concentrations (2 M, 4 M, 6 M and 8 M) at room temperature for 14 h.

c. Cu$_2$O/FTO

Cu/FTO film was put into a glass bottle (volume: 100 ml) containing a solution of 20 ml 4 M NaOH; then the bottle was sealed by a cap and heated on a hot plate to 80 °C. After heating around 1 h, the bottle was taken away and keeping at room temperature for 5 days.

2. Characterization

X-ray diffraction (XRD, Rigaku miniFlex-II desktop, Cu-Kα radiation with $\lambda = 0.154056$ nm) patterns, high resolution transmission electron microscope (HRTEM) and selected area electron diffraction (SAED, JEOL JEM-2100 F) pattern were used to check crystallinity and crystal structure. Surface and cross-sectional morphologies of the films were obtained using a Hitachi Horiba S-4300 scanning electron microscope (SEM) operated at 20 kV. The surface element binding energy and surface composition were characterized by a Thermo VG Scientific (England), Multitab 2000 X-ray photoelectron spectrometer (XPS). The emission peak positions of XPS spectra were corrected using the C1s peak position at 284.5 eV as a reference. A ramé-hart Model 200-F1 contact angle measurement instrument was used for the wettability measurement. The water droplet (ca. 6 μL) is shot to the sample surface by a microliter scale syringe. Photoelectrochemical measurements were conducted with potentiostat PL-9 in a conventional three-electrode cell in a V-style with quartz window cell at room temperature under 1 sun (Asahi HAL-320 sun simulator) illumination, employing a coiled Pt wire and an Ag/AgCl electrode as counter and reference electrode, respectively. Photocurrent-potential was measured using linear sweep voltammogram (LSV) with a scan rate of 10 mV/s under chopped (light on and off: 1 s) 1 sun light. Photoresponses were measured by using
chronoamperometry method at constant potentials of 0 and -0.6 V vs. Ag/Ag/Cl (light on and off: 20 s). A 0.5 M Na₂SO₄ was used as electrolyte solution in all photoelectrochemical properties checking.

3. The growth mechanism of Cu to Cu₂O in NaOH solution:

   It is a well-known phenomenon that the copper can be oxidized in air or under humid conditions; the rate of oxidation is very slow due to the passivation of the surface by the formation of an oxide layer.[2,3] According to the ref. [3] and ref. [4], in presence of alkali solutions, this spontaneous oxidation can be accelerated drastically. Cu²⁺ ions are released continuously from the Cu foil into the alkali solutions (for example, NaOH) while the naturally dissolved O₂ or oxidant ((NH₄)₂S₂O₈) is reduced. The released Cu²⁺ ions can be immediately captured through the coordination with OH⁻ to form Cu(OH)₄²⁻. The possible reaction processes can be carried out as shown the following according to:

   \[2Cu + O_2 + 2H_2O \rightarrow 2Cu^{2+} + 4OH^-;\]

   or \[Cu + S_2O_8^{2-} \rightarrow Cu^{2+} + 2SO_4^{2-}\] (if oxidant exists) \hspace{1cm} (1)

   \[Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2\] \hspace{1cm} (2)

   \[Cu(OH)_2 + 2OH^- \rightarrow Cu(OH)_4^{2-}\] \hspace{1cm} (3)

   Cu(OH)_2 can be readily transformed to monoclinic CuO at low temperature of 60 °C;[5] the Cu(OH)_4²⁻ complex ions can be also dehydrated into CuO in the hot alkaline solution.

   \[Cu(OH)_2 \rightarrow CuO + H_2O\] \hspace{1cm} (4)

   \[Cu(OH)_4^{2-} \rightarrow CuO + H_2O + 2OH^-\] \hspace{1cm} (5)

   If the reductant (such as N₂H₄ or glucose) exists, the final product can be Cu₂O as the following equations.[5,6]

   \[2Cu(OH)_4^{2-} + C_5H_{11}O_2-CHO \rightarrow Cu_2O + C_5H_{11}O_5-COOH + 4OH^- + 2H_2O\] \hspace{1cm} (6)

   \[4Cu(OH)_2 + N_2H_4 \rightarrow Cu_2O + 6H_2O + N_2\] \hspace{1cm} (7)

   The above processes of the formation of Cu₂O can describe the reactions containing alkali and reductant appropriately. However, they cannot explain our experiment because there is no any
additional reductant. Based on the description as above and ref. [7], the possible reaction processes are given as following:

The Cu foil or Cu/FTO can continuously release Cu$^{2+}$ ions into NaOH solution by the naturally-dissolved O$_2$ oxidization.

$$2Cu + O_2 + 2H_2O \rightarrow 2Cu^{2+} + 4OH^-$$ (1)

Then a certain amount of Cu$^+$ can be produced by the process

$$Cu^{2+} + Cu \rightarrow 2Cu^+.$$ (8)

The maximum concentration of [Cu$^+$] is determined by the relationship

$$\log[Cu^+]_{max} = -0.84 - pH.$$ [7] (9)

If the real Cu$^+$ concentration exceeds [Cu$^+$]$_{max}$ given by Eq. (9), the following process will happen.

$$2Cu^+ + 2OH^- \rightarrow Cu_2O + H_2O$$ (10)

The transformation of Cu to Cu$_2$O in our experiment may be carried out by the net reaction as follows:

$$4Cu + O_2 \rightarrow 2Cu_2O.$$ (11)
**Fig. S1** (a and b) Low magnification SEM images, (c) TEM image and (d) SAED pattern of Cu$_2$O/Cu$_1$ obtained by adding Cu$_1$ foils in 20 ml 4 M NaOH aqueous solution followed by heating at 80 °C for around 1 h and then keeping at room temperature for 4 days.

The Fig S1(a) and (b) show the film is uniform in large area scale. There are a few big particles with the size from ~3 μm to ~5 μm as show in Fig. S1(b). The size of most particles is in the range of ~1 μm to ~2 μm as shown in Fig. S1(c). The average particle size is < 1.5 μm. The SAED pattern can be indexed to cubic phase Cu$_2$O (JCPDS no. 65-3288) as a similar result obtained by Mao *et al.*[8]
Fig. S2 (a) Low magnification top-view and (b) cross-sectional SEM image of Cu$_2$O/Cu$_2$ obtained by adding Cu$_2$ foils in 20 ml 4 M NaOH aqueous solution of 80 °C then kept at room temperature for 14 h.
Fig. S3 Low and high magnification SEM images of Cu$_2$O/Cu$_2$ films obtained by adding Cu$_2$ foils in 20 ml NaOH aqueous solution of 80 °C with different concentrations then kept at room temperature for 14 h. (a and b) 2 M, (c and d) 6 M and (e and f) 8 M.
Fig. S4 Low and high magnification SEM images of Cu₂ foil (2 cm × 2 cm) surfaces after keeping Cu foil in 20 mL NaOH aqueous solution with different concentrations at room temperature for 14 h. (a and b): 2 M; (c and d): 4 M; (e and f): 6 M; (g and h): 8 M.
Fig. S5 Low and high magnification SEM images of Cu₂ foil (2 cm × 2 cm) surfaces after keeping Cu foil in 20 mL 2 M NaOH aqueous solution of 80 °C and then kept at room temperature for different time. (a and b): 28 h; (c and d): 60 h; (e and f): 20.5 days.

The Cu₂O film can be converted to CuO when the immersion time was extended. After immersion for 60 h, the morphologies of Cu₂O were changed from polyhedron to normal grain shape. After 20.5 days, the cabbage-like CuO was formed as the similar result reported by Liu at al.\textsuperscript{[9]} Herein, our results indicate that the change process of Cu in NaOH solution is as the following:

\[
\text{Cu} \rightarrow \text{Cu}_2\text{O} \rightarrow \text{CuO}
\]
The Cu foil can be oxidized to Cu$_2$O/Cu and further to CuO-Cu$_2$O/Cu or CuO/Cu.

Fig. S6 (a) is a 26-facet polyhedral architecture with exposed \{111\} \times 8, \{100\} \times 6 and \{110\} \times 12 facets. (b-f) SEM images at different area with different magnifications of Cu$_2$O/Cu$_2$ after checking photocurrent-potential and photoresponse.
Fig. S7 (a) Low and (b) high magnification SEM images of Cu/FTO obtained by electrodeposition of a solution containing 25 ml 0.1 M Cu(NO$_3$)$_2$ and 3 M lactic acid at pH 5 for 10 min with applied potential of -0.4 V vs. Ag/AgCl as our previous report.$^{[1]}$

Reference