Supplementary Information for:

One-step fabrication of highly conductive and durable copper paste and its flexible dipole tag-antenna application

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1. Experimental Section

Synthesis of poly (VI-co-VTS): Poly(VI-*co*-VTS) was synthesized by free radical copolymerization using a,a′-azobisisobu-tyronitrile (AIBN) as an initiator. VI (Sigma-Aldrich, 9 mL) and VTS (Sigma-Aldrich, 1 mL) were copolymerized in 2-propanol (100mL) at 60 °C with stirring in nitrogen atmosphere. The total monomer concentration was 1M, and the initiator concentration was fixed at 1×10^{-3} M. The mole ratios of the two monomers in the feed were 9 : 1. The polymerization was initiated with AIBN (0.01 g) for 12 h at 60 °C. After the reaction period required for copolymerization, the contents were pippeted, immediately precipitated by a large volume of 2-propanol (100 mL). The precipitated copolymers were collected by filtration, washed with 2-propanol and finally dried in a vacuum oven.

Preparation of PSS: PSS was synthesized by radical polymerization in an aqueous solution at 50 °C. The 4-styrenesulfonate sodium salt (Sigma-Aldrich, 2 g) was introduced into distilled water (40 mL) and stirred vigorously for 2 h. The polymerization of styrenesulfonate was initiated with AIBN (0.06 g) for 6 h at 50 °C, resulting in an aqueous PSS solution.

One step method to prepare the highly conductive and durable Cu paste: The Cu flake (10 g, Join M Co., Ltd) was added into a mixed solution composed of hydrochloric acid (15 mL), phosphoric acid (30 mL), Poly(VI-*co*-VTS) (10 mL) and 5 mL of PSS solution. The molar concentration of acid was 1 M. After being shaking the Cu paste for 2 h at room temperature, the mixture was precipitated by centrifugation (5,000 rpm, 5 min). Then, grinding process for solid like Cu cake was performed using an agate mortar, and highly conductive and durable Cu paste (10 mL) could be obtained. Commercial Ag paste (Join M Co., Ltd) was also used as screen printing ink, and hardening process was conducted under 150 °C oven for 30 min.

Fabrication of Cu-based dipole tag-antenna using screen printing: A ellipse-like pattern of Cu-based thin film (10 mm inner diameter, 11 mm outer diameter) was formed onto PET film by screen-printing. Fabricated Cu-based dipole antenna electrode was connected to the Network Analyzer using SMA type connector.

Long term and thermal stability test: The long term reliability was tested through checking the variation of surface resistance for 1 month at room temperature. For thermal stability testing, hot pressing process using hot bar was conducted, and the applied temperature and pressure of hot plate were ca. 160 °C and 700 psi, respectively.

Characterization: The Field-emission scanning electron microscope (FE-SEM) images were obtained on a JEOL 6701F. The synthesized Cu paste was investigated by using FTIR spectroscopy (Bomem MB 100). For cutting the Cu-based surface, Focused Ion Beam (FIB, Carl Zeiss AURIGA model) using Ga element was used, and Pt nanoparticles were deposited on the surface by sputtering to distinguish between Cu surface and oxidation protection layer. X-ray photoelectron spectroscopy (XPS) spectra were recorded using Kratos Model AXIS-HS system. For sample preparation, screen printing (Sunmechanix, SM-S550) and PET substrate were used. In the case of XPS deptp profile, Ar ion source of 3 keV was used for etching the thin film, and the velocity of the ion sputtering was estimated to be ca. 1.0 nm/min. Surface energy was calculated using the Owens-Wandt equation, and optical micrographs were acquired with a Leica DM2500 P. Measurements of electrical resistances were performed with a Keithley 2400 source-meter at 25 °C using a four-point probe method. An E5071B ENA RF Network Analyzer from Agilent Technologies was used to characterize the RFID antennas between 300 kHz and 8.5 GHz. Impedance was plotted on a Smith chart by first normalizing to the characteristic impedance of the system (50 ohms).

2. The electrical measurement for three types of Cu thin film

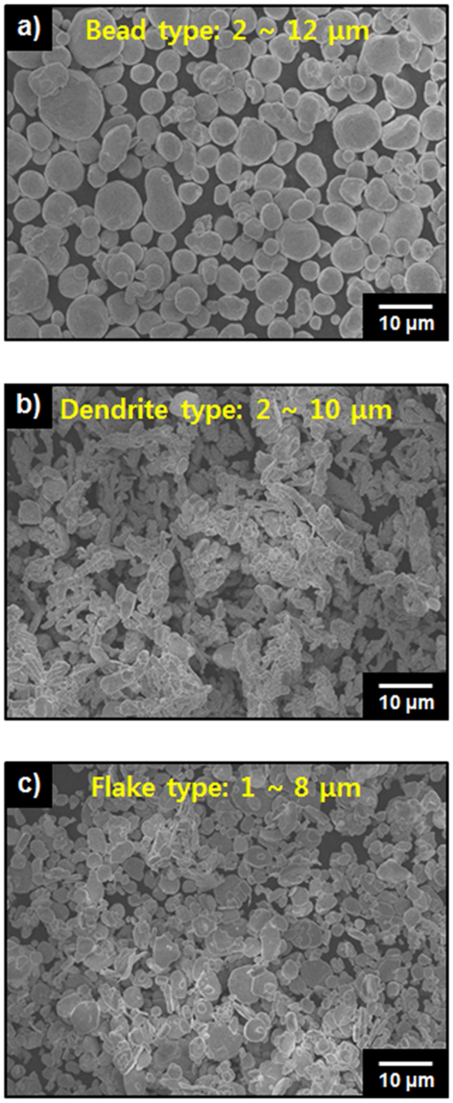

Fig. S1 SEM images showing the a) bead, b) dendrite, and c) flake type of Cu.

Table S1. Surface resistance value for three differnt types of Cu-based thin film

Cu-based thin film	Flake type	Bead type	Dendrite type
Surface resistance (mΩ/sq) [a]	105	230	578

[a] These value were measured by a four probe method and the thickness was *ca.* 30 µm.

3. FTIR spectra of highly conductive and durable Cu paste

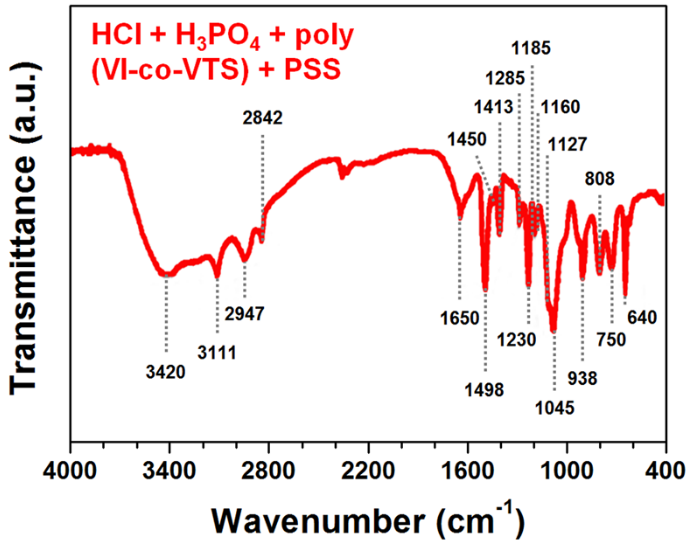

Fig. S2 FTIR spectra of highly conductive and durable Cu paste. Powdered samples were used for FTIR analysis.

Table S2. Tentative band assignments of highly conductive and durable Cu paste.

Band positions (cm^{-1}) [a]	Tentative assignmets
3420	O-H from residual water
3111	C=C-H/N=C-H stretching
2947	CH_3 asymmetric stretching from Si-O-CH_3
2842	CH_3 symmetric stretching from Si-O-CH_3
1650	O-H deformation(water)/C=N stretching
1498	C=C/C=N stretching
1450	CH_2 bending(mostly) + ring stretching
1413	CH_2 bending(mostly) + ring stretching
1285	Ring vibrations
1230	Ring vibrations
1185	Asymmetric stretching of the sulfonic group
1160	P=O of the phosphate group
1127	In-plane skeleton vibration of the benzene ring
1045	Symmetric stretching of the sulfonic group
938	O-P-O of the phosphate group
808	CH out-of-plane bending + Si-O-C symmetric stretching
750	CH_2 bending
640	P-O of the phosphate group

[a] The FTIR Spectra were obtained using Bomem MB-100 spectrometer at a resolution of 4 cm^{-1} and 16 scans were collected. The spectrometer was continuously purged with nitrogen gas to remove water vapor and atmospheric CO_2.

4. The cross section images of various Cu paste

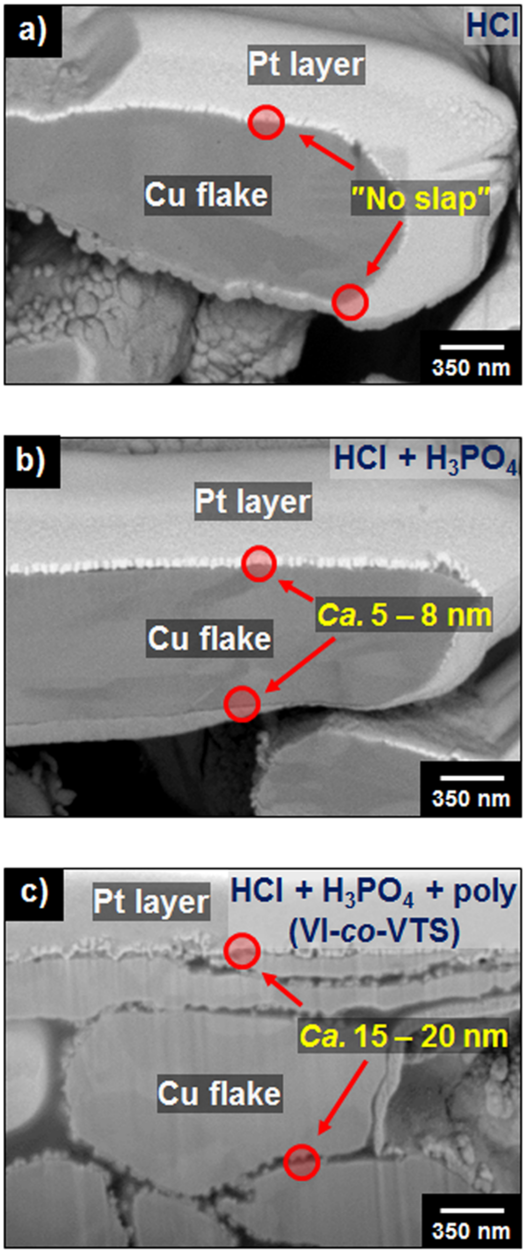

Fig. S3 Representative SEM images showing the cross section of a) HCl, b) HCl/H_3PO_4, and c) HCl/H_3PO_4/poly(VI-*co*-VTS). For cutting the Cu-based surface, FIB using Ga element was used, and Pt nanoparticles were deposited on the surface by sputtering to distinguish between Cu surface and oxidation protection layer.

5. Cu $2p_{2/3}$ and O 1s XPS analysis for Cu-based thin films

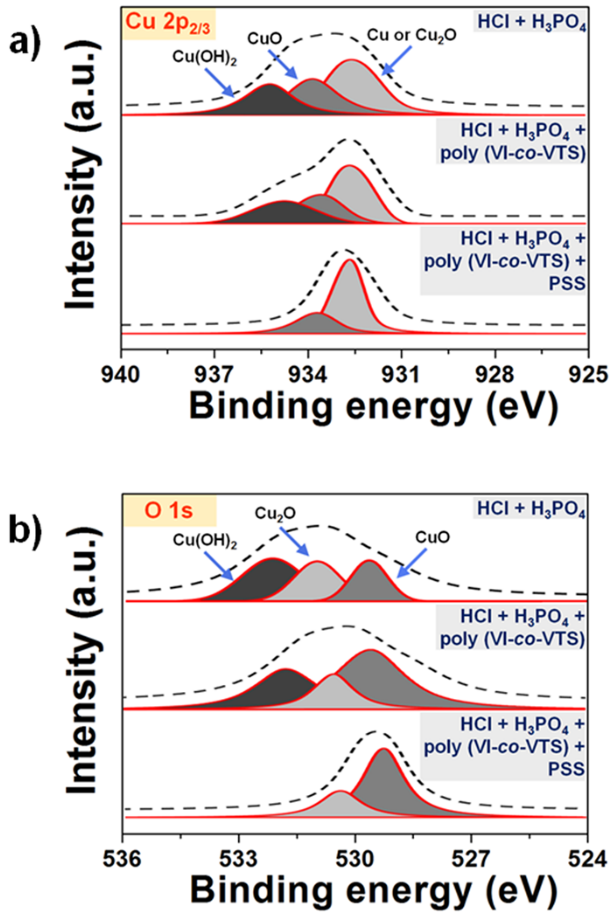

Fig. S4 Deconvoluted XPS spectra for three different types of Cu-based thin films in a b) Cu $2p_{2/3}$ and c) O 1s peaks.

In order to confirm the protection from oxidation on Cu flake surface, Cu $2p_{2/3}$ and O 1s XPS analysis of Cu-based thin film was conducted. Generally, the Cu $2p_{3/2}$ signal mainly consists of three components, which are to Cu or Cu_2O (932.6 eV), CuO (933.7 eV), and $Cu(OH)_2$ (935.1 eV) peaks (Fig. S3a). It is found that the intensity ratio of the CuO and $Cu(OH)_2$ peaks to Cu or Cu_2O has decreased with phosphoric acid treatment and addition of poly(VI-*co*-VTS) (Table S2). Most of all, as a result of PSS layer, the ratio of the $I_{CuO}/I_{Cu\ or\ Cu2O}$ has highly reduced, and the $Cu(OH)_2$ peak has disappeared. However, it is difficult to distinguish metallic Cu peak from Cu_2O peak because of the small shift 0.1 eV. For this reason, O 1s XPS analysis was also performed. Figure S3b shows that the O 1s spectra can be separated into peaks at 529.4, 530.6, and 532.1 eV, which are assigned to CuO, Cu_2O, and $Cu(OH)_2$, respectively. The intensity ratio of Cu_2O to CuO peak has decreased by addition of corrosion inhibitors, and $Cu(OH)_2$ peak has also disappeared, which agrees with the Cu $2p_{3/2}$ spectra. From the data, the ratio of I_{Cu2O}/I_{Cu} could be measured, and the value has highly reduced (0.11). As a result, the relative atomic ratio of O to Cu element has also decreased from 1.72 to 0.42 by addition of corrosion inhibitors, leading to an outstanding resistance to oxidation.

Table S3. The peak intensity ratio for four different Cu-based thin films.

ratio [a]	HCl	HCl + H_3PO_4	HCl + H_3PO_4 + poly (VI-*co*-VTS)	HCl + H_3PO_4 + poly (VI-*co*-VTS) + PSS
$Cu(OH)_2$/CuO	0.71	0.56	0.41	-
CuO/(Cu or Cu_2O)	0.87	0.64	0.52	0.32
Cu_2O/CuO	0.81	0.78	0.48	0.30
Cu_2O/Cu	2.33	0.75	0.33	0.11
O/Cu	1.72	1.15	0.70	0.42

[a] These values were acquired by integrate function of OriginPro software (OriginPro 7.5, Originlab corporation, USA) in order to calculate the area of peak intensity.

6. Optical image of patterned Cu-based thin film

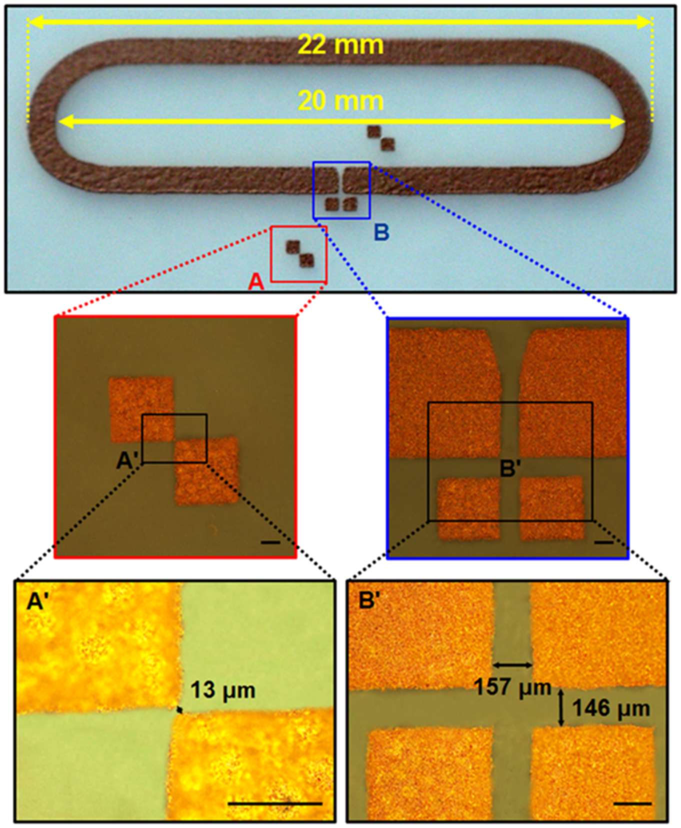

Fig. S5 Optical images showing the patterned Cu-based thin film. The optical images are magnified at the marked areas (scale bar: 150 μm). The designed distances along the diagonal direction for the A section and horizontal direction for the B section were 20 μm and 150 μm, respectively.

Synthesized Cu paste could be used as screen printing ink, allowing its application for dipole tag-antenna electrode. The optical images of patterned Cu-based thin film on a flexible substrate are displayed (Fig. S4). In our experiment, ellipse-like patterns (10 mm internal diameter and 11 mm outer diameter) have been formed on poly(ethylene terephthalate) (PET) film, and flip-chip bonding locations are specified along sections A and B. The optical images of section A and B formed demonstrate well-defined pattern, and it could be attributed to the surface energy matching between the substrate and Cu paste. Namely, the surface tension of Cu paste was measured to be ca. 61.07 mN m^{-1} by the Owens-Wendt equation, which was similar to that of PET film (65.12 mN m^{-1}), resulting in an excellent compatibility with respect to the substrate. Therefore, sharp Cu-based pattern could have been obatained without line-edge waves after Cu paste transferred to the substrate.

7. The electrical measurement of Ag and Cu-based thin films

a)

b)

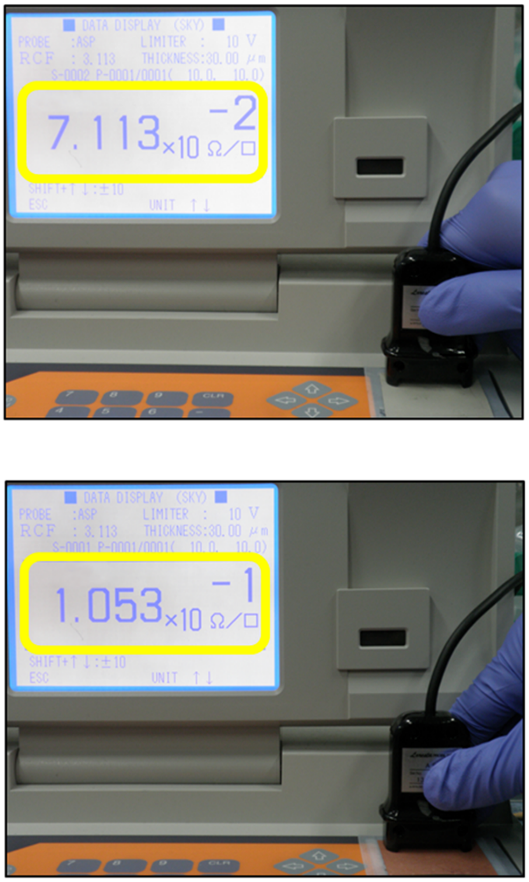

Fig. S6 The electrical measurement of the a) Ag and b) Cu-based thin films by using the 4-probe method.

8. Photo images of oxidized and highly durable Cu thin film

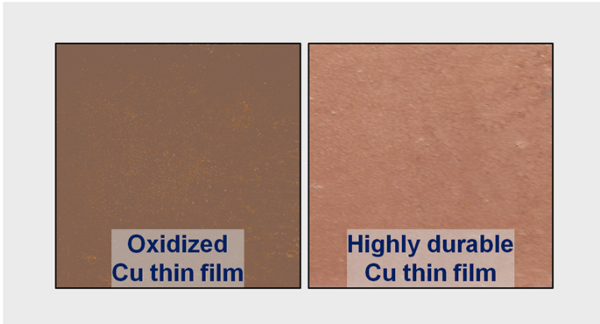

Fig. S7 The surface photo image of oxidized and highly durable Cu thin films using screen printing after 1 month at room temperature.

9. Cu-based dipole tag-antenna application

Table S4. *VSWR*, *RL* and *TP* values of Cu-based dipole tag antenna.

VSWR	Return Loss (*RL*) [a]	Reflection Coefficeint (Γ)	Transmitted Power (*TP*)	Reflected Power
1.19	21.2	0.033	99.2	0.8

[a] These values were acquired in the E5071C ENA RF Network Analyzer of Agilent Technologies.