

Supporting information

The polymeric nanofilm of triazinedithiolsilane capable of resisting corrosion and serving as an activated interface on copper surface

Yabin Wang,^{ab} Zhong Liu,^b Yaping Dong,^b Wu Li,^b Yudong Huang^{*a}, Yutai Qi^{*a}

^a School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, P. R. China. E-mail: ydhuang.hit1@aliyun.com; inqdsd@yahoo.com.cn. Tel.: +86 451 86414806; fax: +86 451 86221048.

^b Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining, Qinghai 810008, P. R. China.

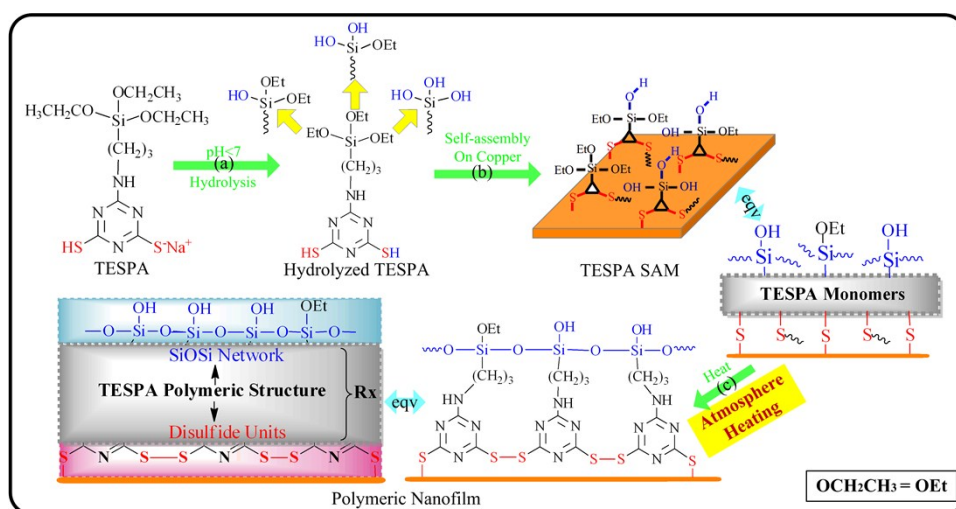


Fig. S1 The preparation process of TESPAs polymeric nanofilm fabricated by self-assembled technique on copper surface. Triethoxysilyl groups in TESPAs first hydrolyze to yield silanol groups (a), then the hydrolyzed TESPAs molecules self-assemble onto copper surface (b), finally the SH groups polymerize and SiOH groups lose water to produce polymeric nanofilm with protective structures when heated (c). R_x between the two textures can be altered by the molecular chain length.

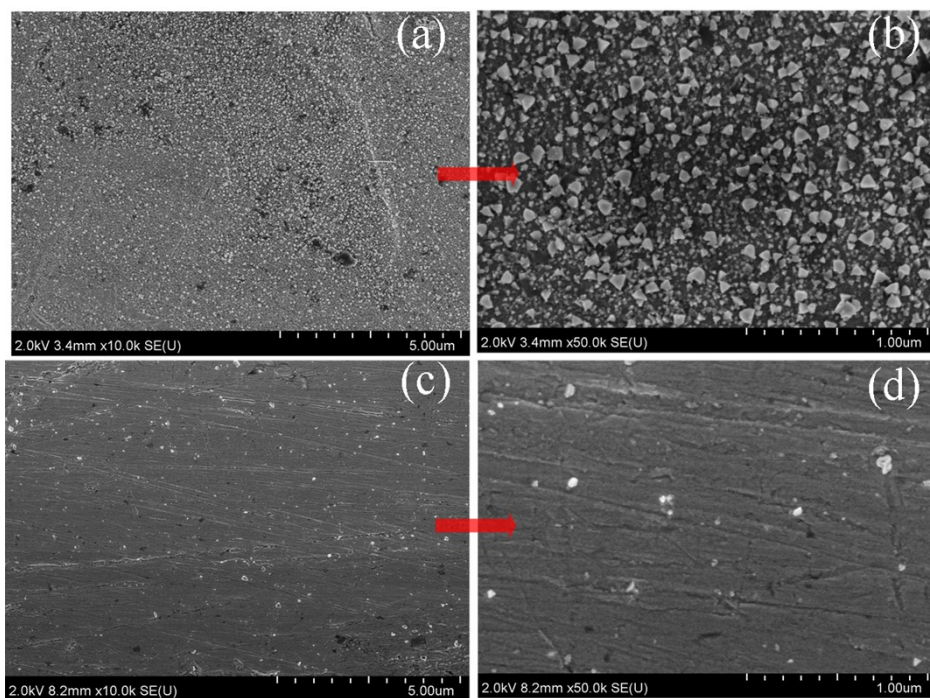
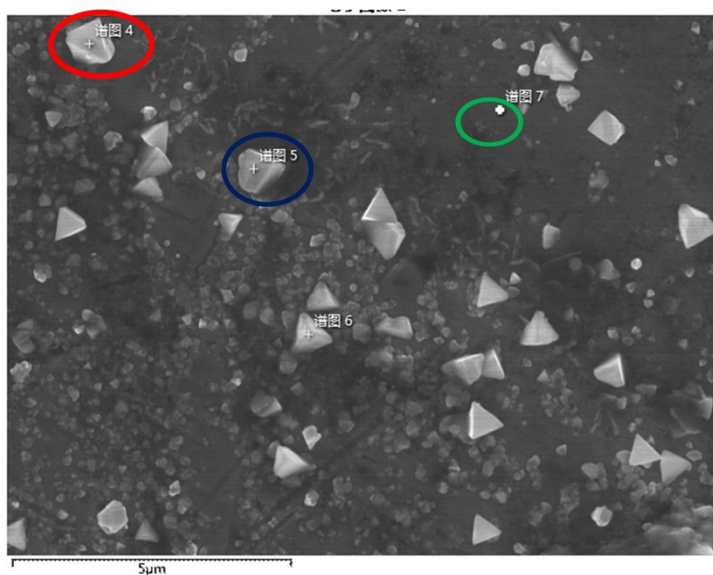


Fig. S2 SEM images of copper surface modified directly by OTS with 5 μm (a) and 1 μm (b); SEM images of the bare copper surface with 5 μm (c) and 1 μm (d). It is clear that lots of amorphous white particles (Figure S2b) emerge and distributed on the copper surface (Figure S2a). The copper surface is seriously destroyed compared with the bare one (Figure S2c and Figure S2d). Thus, the direct anchoring of OTS causes serious corrosion on copper substrate.



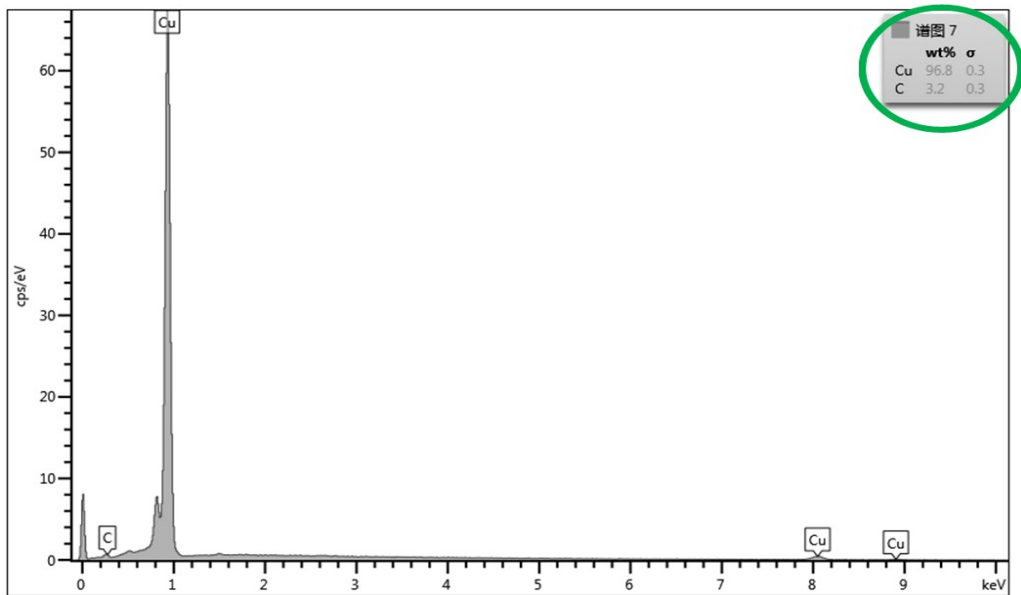
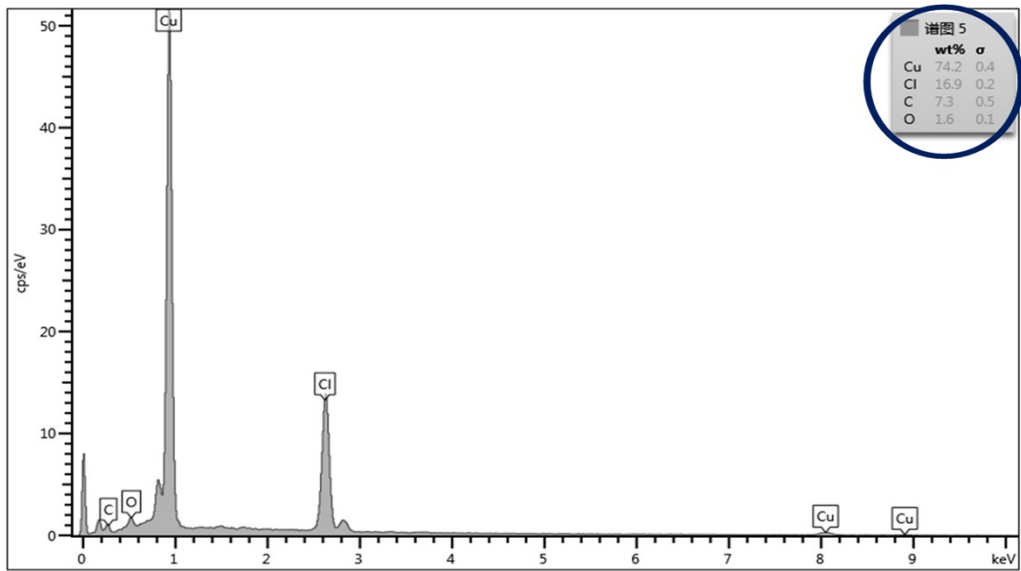
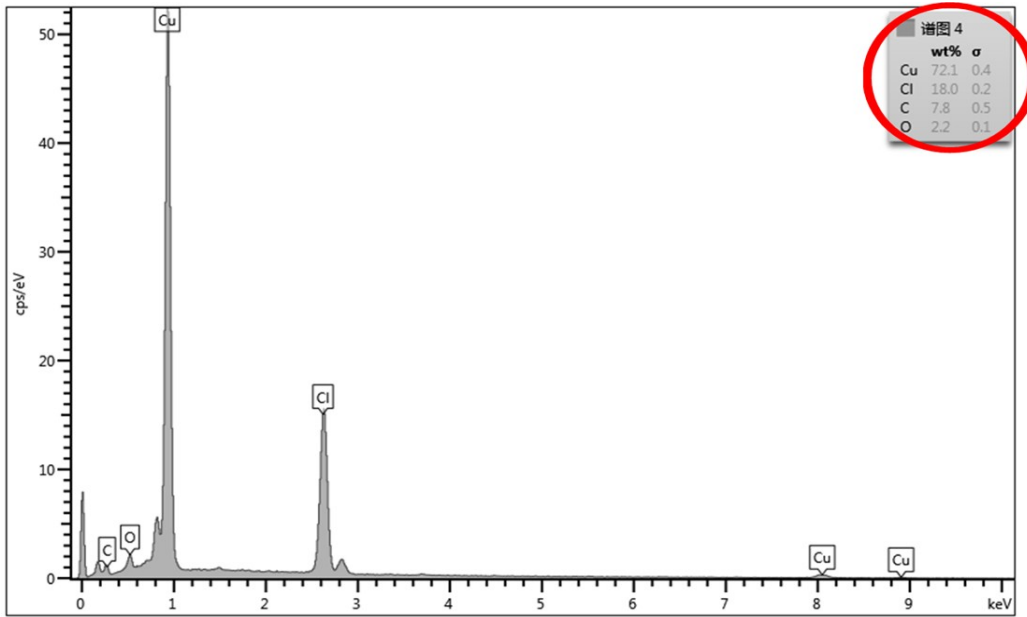


Fig. S3 The nature of the white particles from copper surface modified directly with OTS. Chlorine with high content exists in the white particles (4 in red circle and 5 in blue circle), and the surface without the white particles excludes Cl (7 in green circle), which demonstrates that the white particles are the products of reaction between copper and OTS. The bare copper surface is seriously destroyed by direct modification with OTS.

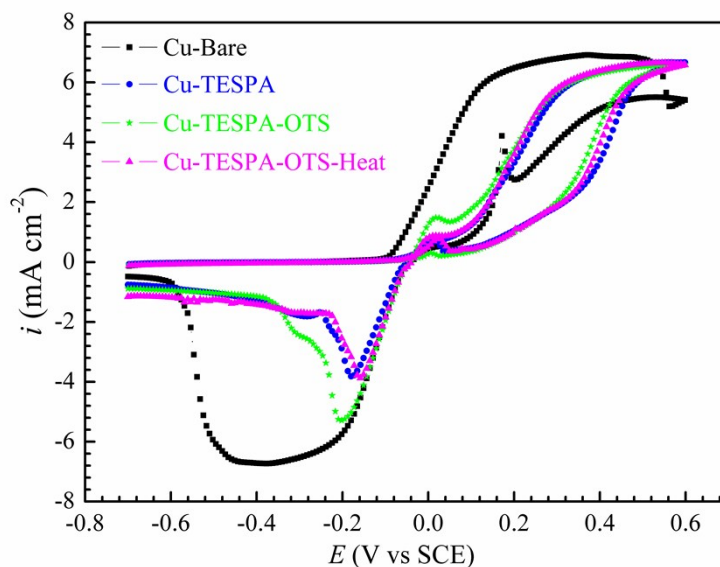


Fig. S4 Cyclic voltammograms of the bare copper (Cu-Bare), copper treated with TESPA (Cu-TESPA), TESPA-coated copper modified with OTS (Cu-TESPA-OTS), and TESPA-coated copper modified with OTS plus following heating (Cu-TESPA-OTS-Heat) in 3.5 wt% NaCl solution. Cu-TESPA stands for copper surface covered with TESPA SAM.

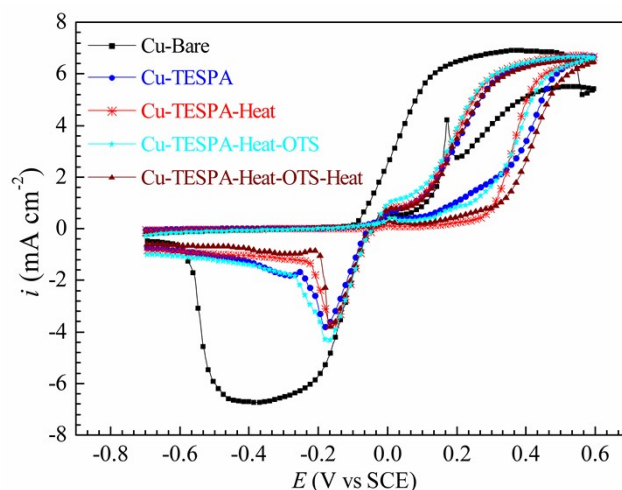


Fig. S5 Cyclic voltammograms of the bare copper (Cu-Bare), copper treated with TESPA (Cu-TESPA), copper treated with TESPA plus the following heating (Cu-TESPA-Heat), TESPA-coated copper modified with OTS (Cu-TESPA-Heat-OTS), and TESPA-coated copper modified with OTS plus the following heating (Cu-TESPA-Heat-OTS-Heat) in 3.5 wt% NaCl solution. Cu-TESPA stands for copper surface covered with TESPA SAM, and Cu-TESPA-Heat represents copper surface covered with TESPA polymeric nanofilm.

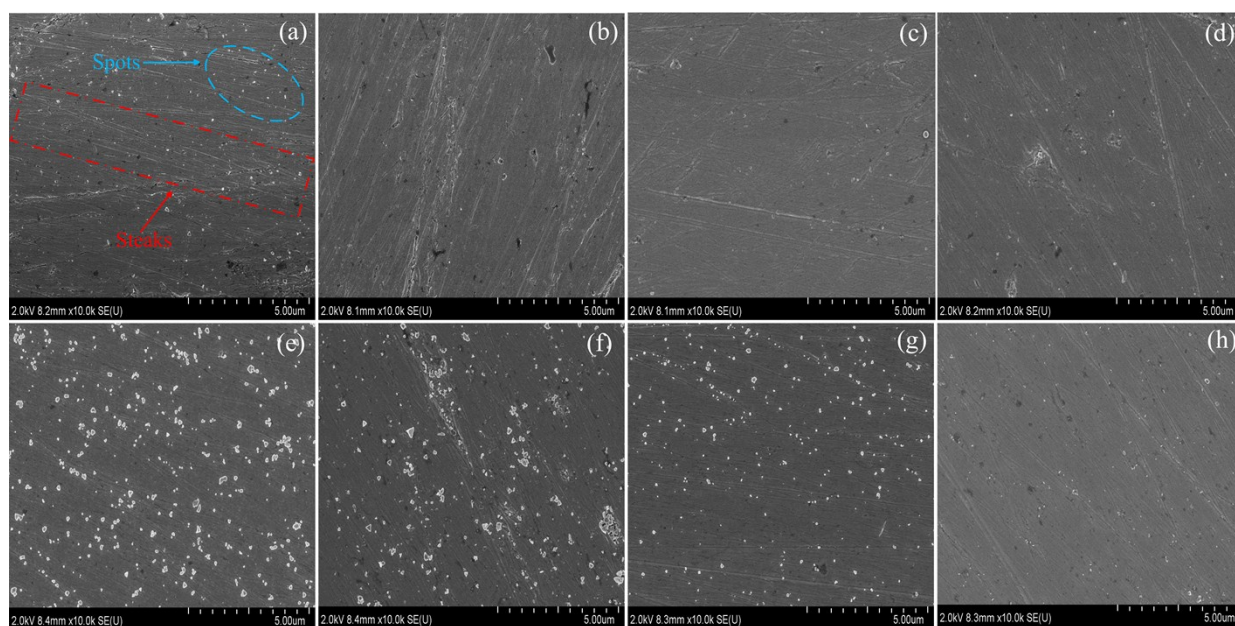
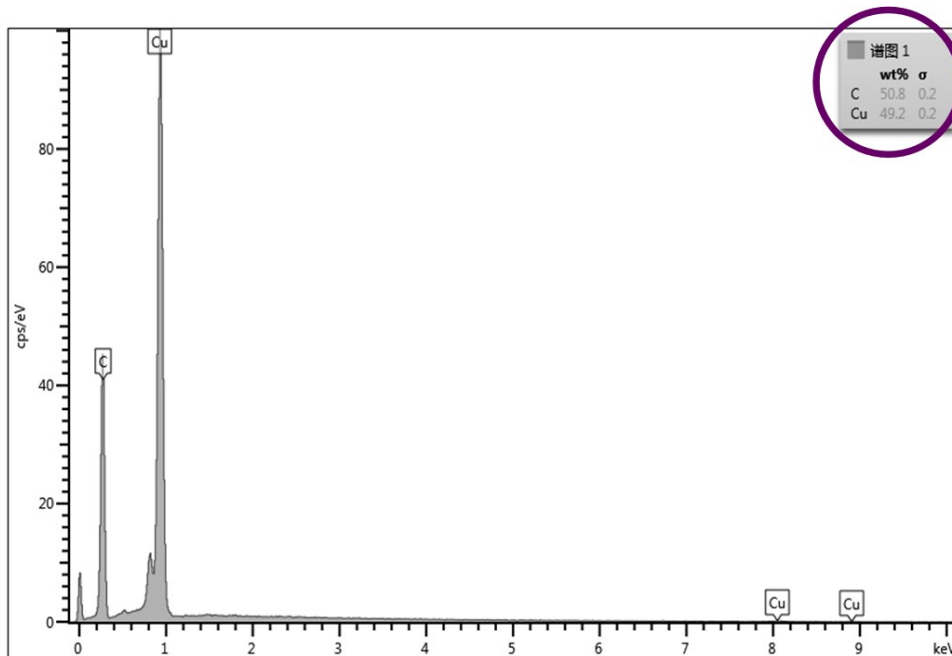
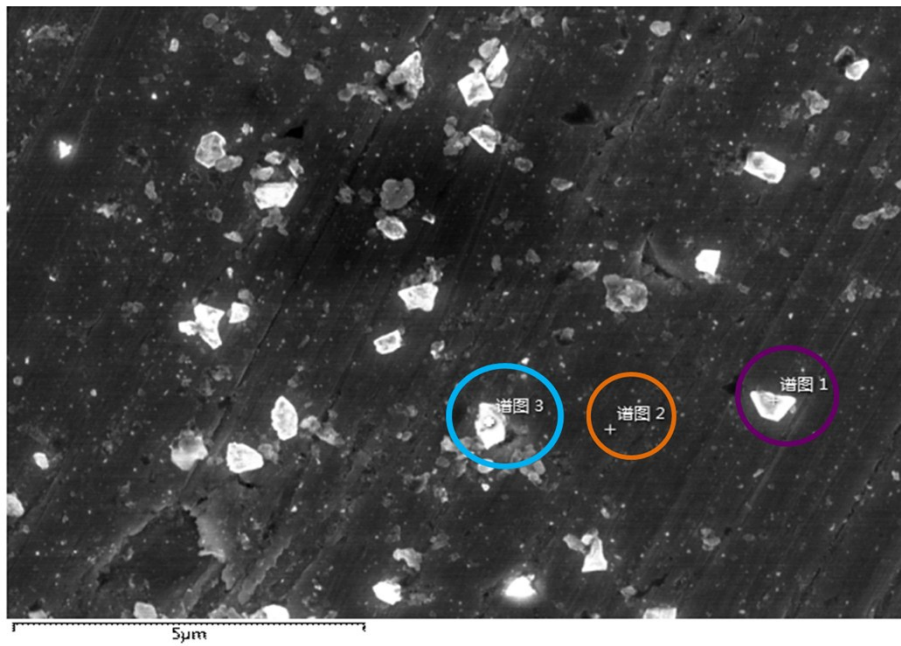


Fig. S6 SEM micrographs with 5 μm of the (a) bare copper, (b) heated copper, (c)

copper treated with TESPA, (d) copper treated with TESPA plus following heating, (e) OTS-modified TESPA SAM without heating, (f) OTS-modified TESPA SAM plus heating, (g) OTS-modified TESPA polymeric nanofilm without heating, and (h) OTS-modified TESPA polymeric nanofilm plus heating.



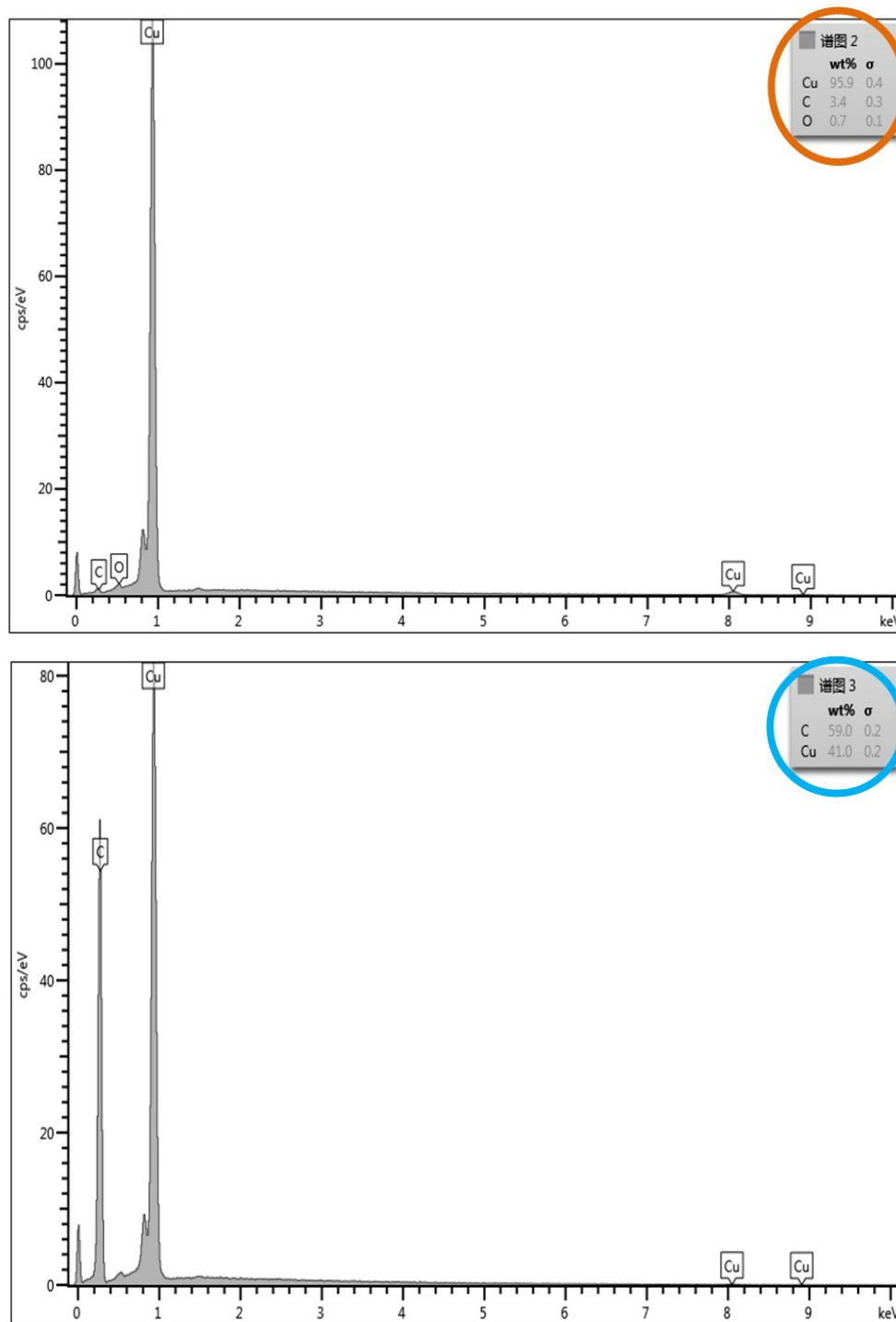
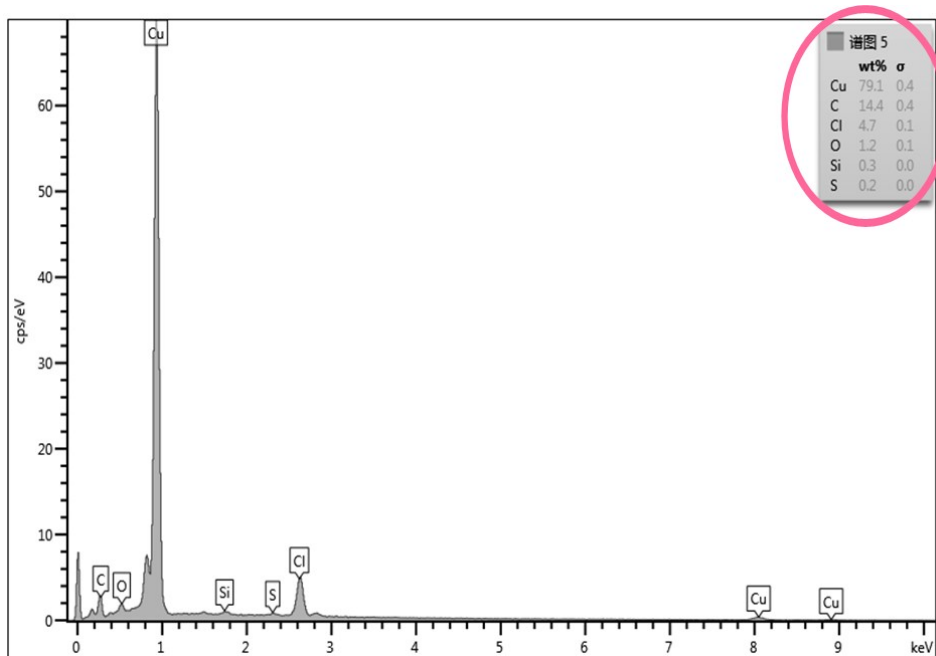
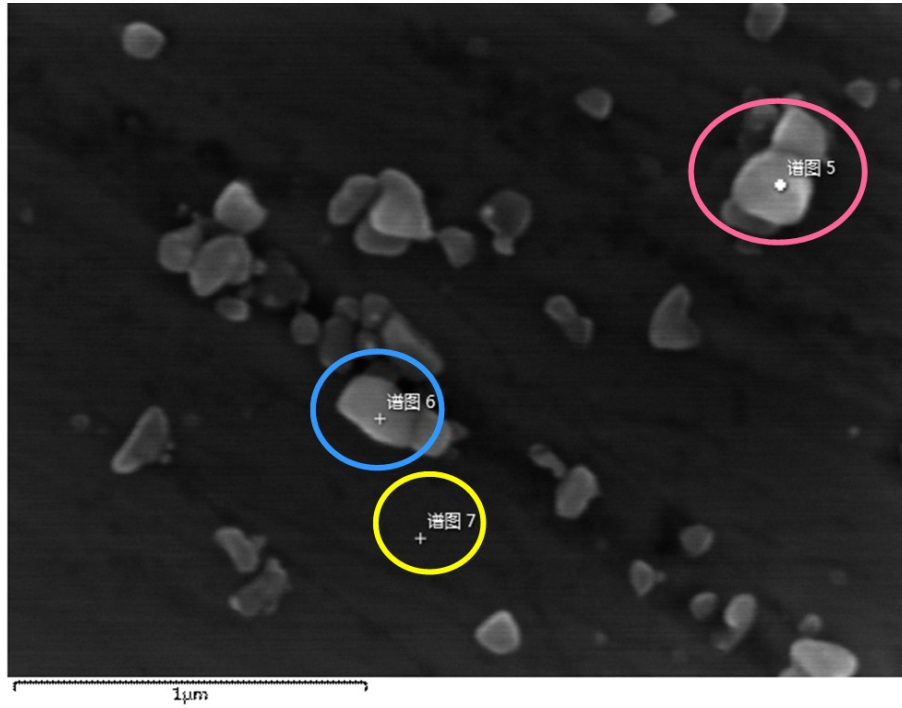


Fig. S7 The nature of the white spots from bare copper surface. The copper surface was roughly polished to obtain white spots as many as possible. Then, the surface was thoroughly rinsed with acetone, alcohol and pure water accompanied with ultrasonic. From EDS results, the white spots have higher carbon content (1 in purple circle and 3 in indigo circle) than that of the flat surface (2 in golden circle).

We can confirm that the white spots are solely “carbon contaminations” from fabricating procedure.



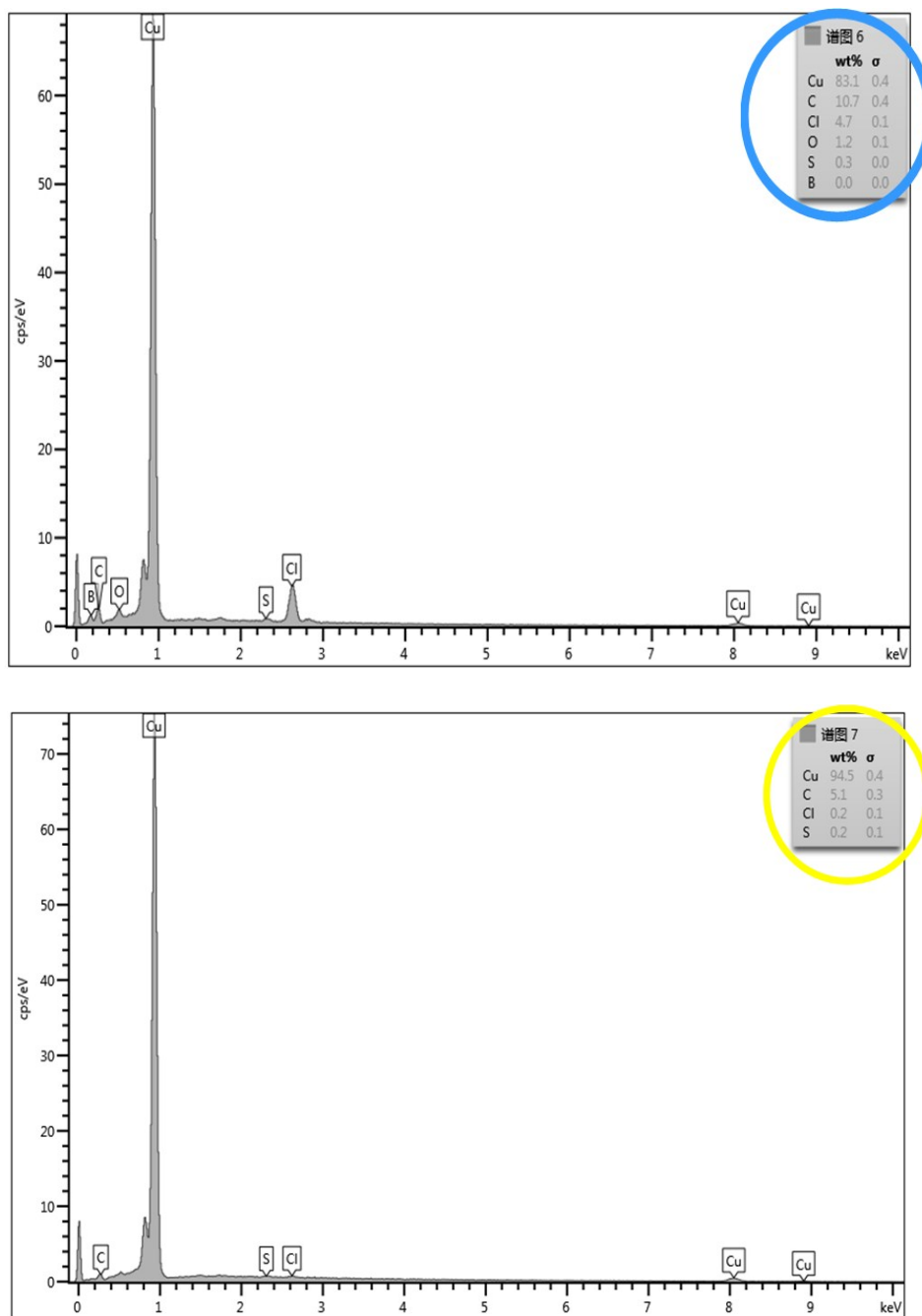


Fig. S8 The nature of the white particles from TESPA SAM-covered copper surface modified with OTS. The white particles have high content of chlorine (5 in pink circle and 6 in sky blue circle), while the flat sites are mainly TESPA film (7 in yellow circle). These observations manifest not only that the white particles are the products of reaction between TESPA and OTS, but also TESPA SAM primarily reacts with

OTS and protect the copper substrate.

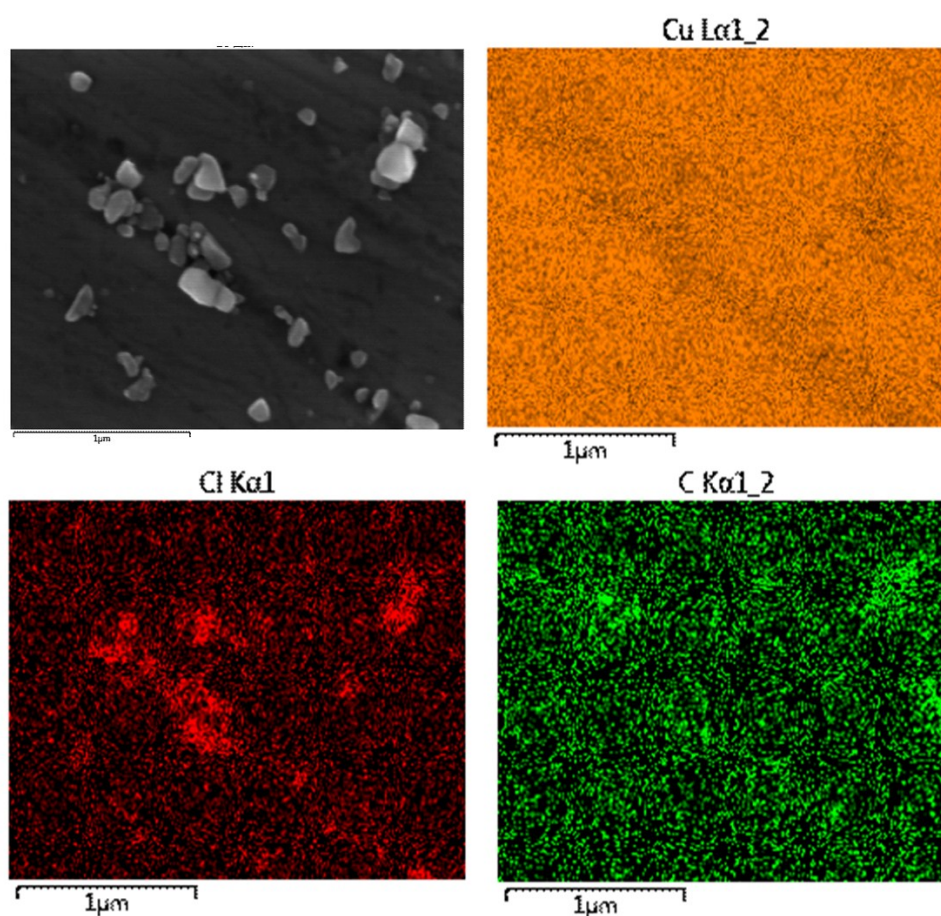


Fig. S9 The element mapping of the white particles from TESPAM SAM-covered copper surface modified with OTS. It clearly reveals that Cl and C elements are highly contained in the particles (the red Cl K α 1 and the green C K α 1_2). Copper surface without particles are uniformly covered by bilayer of TESPAM and OTS (the golden Cu L α 1_2). These observations supplement that the white particles are the products of reaction between TESPAM and OTS. Further, TESPAM SAM primarily reacts with OTS and protect the copper substrate.

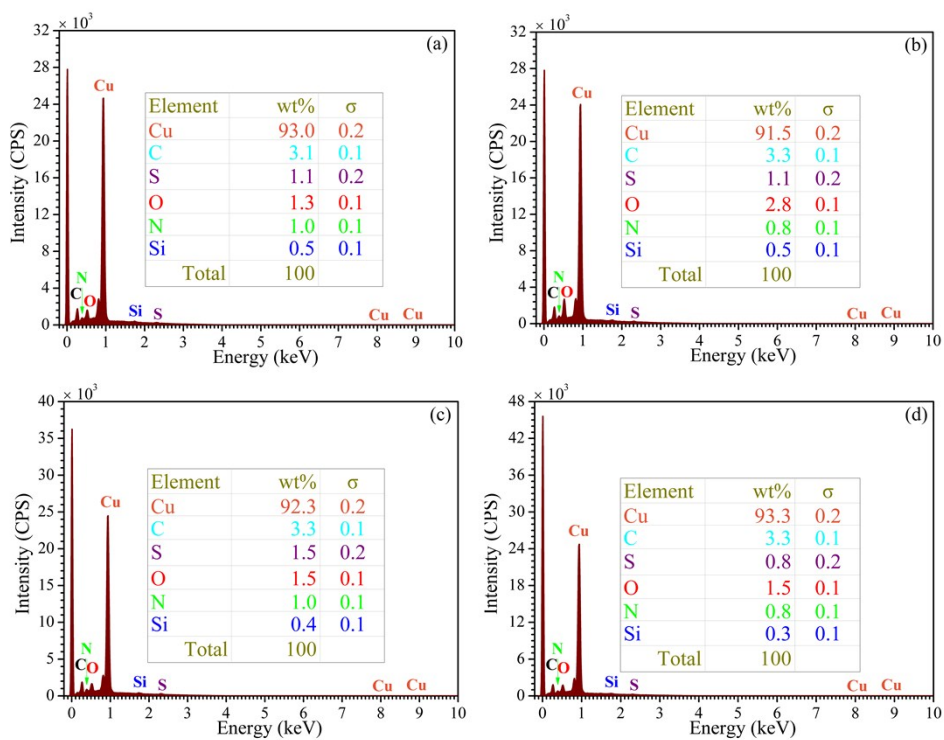


Fig. S10 EDS spectra of the (a) OTES-modified TESPAs SAM without heating, (b) OTES-modified TESPAs SAM plus heating, (c) OTES-modified TESPAs polymeric nanofilm without heating, and (d) OTES-modified TESPAs polymeric nanofilm plus heating.