

Figure S1. Auger electron spectrum of the Cu(111) thin films (100 ML) (a) as deposited and (b) sputtered with Ar for 30 sec. Note that no Pb peak is observed at 245 eV, which indicates that the mediating Pb is not included in the Cu film.

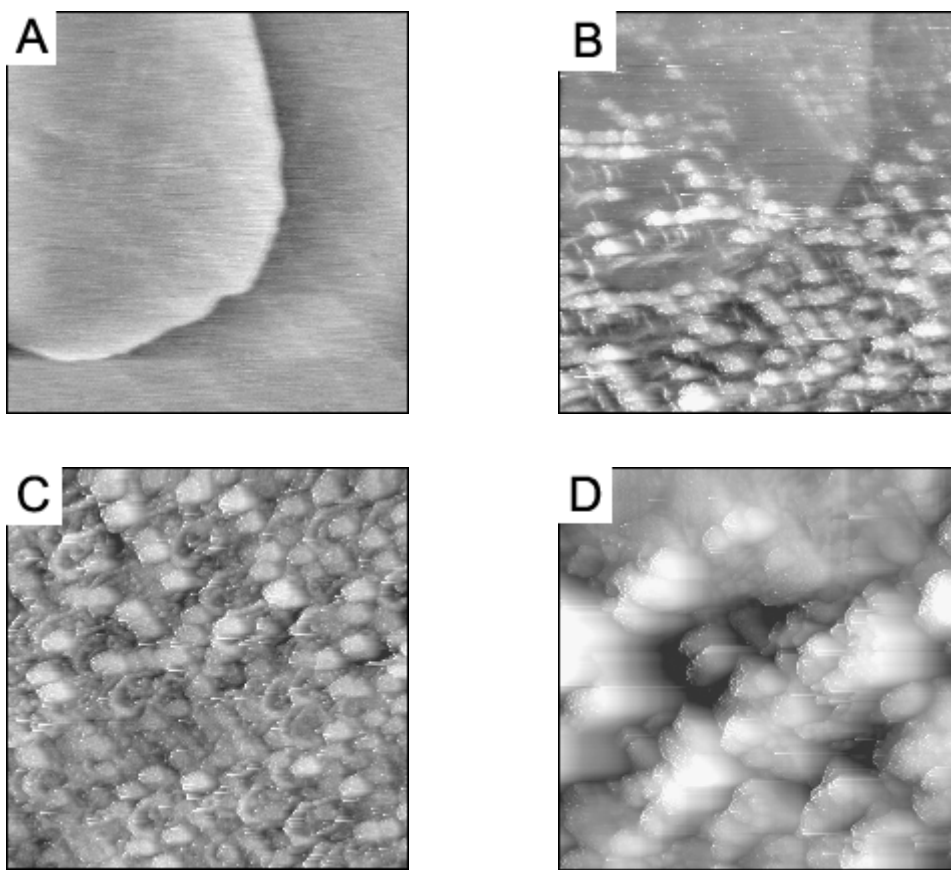


Figure S2. A temporal sequence of *in situ* STM images of Cu electrodeposition on Au(111) without Pb mediator. (a) $280\text{nm} \times 280\text{nm}$ image of the bare Au(111). (b) Growth of mesa-like Cu adlayers after potential was stepped to 0.050 V vs Pb/Pb²⁺. After Fig. S2(b) is acquired, the voltage was stepped back to 0.400 V . And (c) After six 1-s pulses to 0.050 V . (d) Thicker Cu film after 2000 pulses ($280\text{nm} \times 280\text{nm}$). Since experiment should be performed without Pb²⁺, we did not use Pb wire reference. For this experiment, the potentials were measured relative Cu/Cu²⁺.