Supporting Information

Additive-Free Shape-Invariant Nano-to-Micron Size-Tuning of Cu_2O Cubic Crystals by Square-Wave Voltammetry

Xuyun Guo,[1] *Weiqiang Lv,*[1] and *Xiao-Yuan Li*[1,2,3*]

[1]Department of Chemistry, [2]William Mong Institute of Nano Science and Technology,
[3]Energy Institute,
The Hong Kong University of Science and Technology,
Clear Water Bay, Kowloon, Hong Kong SAR, People's Republic of China
* To whom correspondence should be addressed at (852)-2358-7356, Email: chxyli@ust.hk

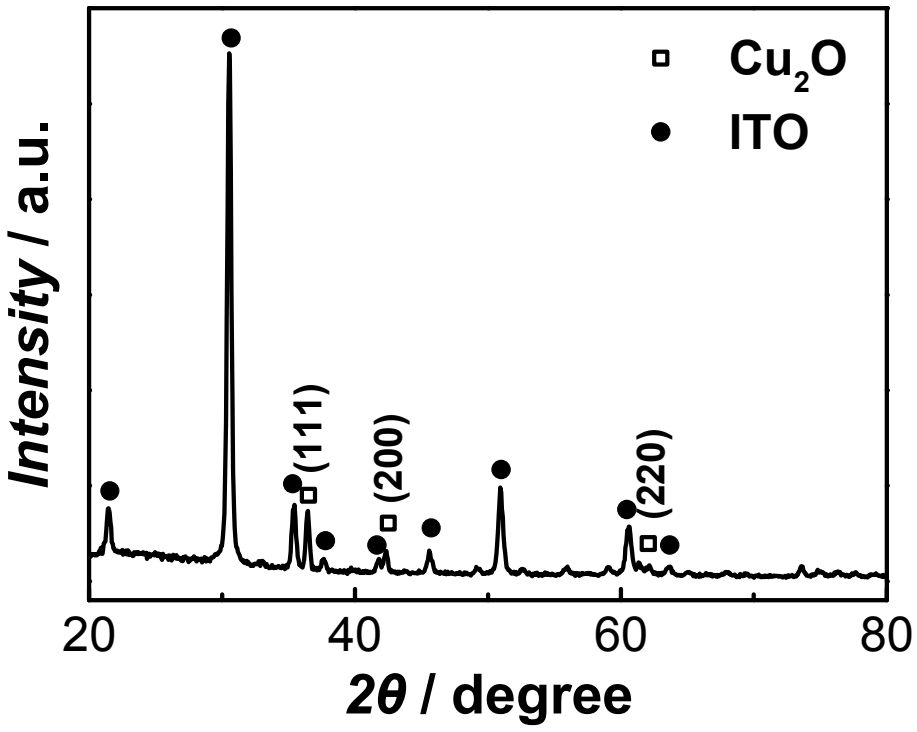

Figure S1. A typical XRD pattern of the as-fabricated Cu_2O crystalline nanocubes electrodeposited on an ITO substrate by SWV. The SWV parameters used are t_0 = 2 s, f = 6 Hz, E_0 = -0.08 V, E_i = -0.08 V, E_f = -0.20 V, ΔE_{step} = -0.333 mV, E_{sw} = 80 mV, N = 20. All peaks are attributable to either Cu_2O crystalline particles or the ITO substrate.

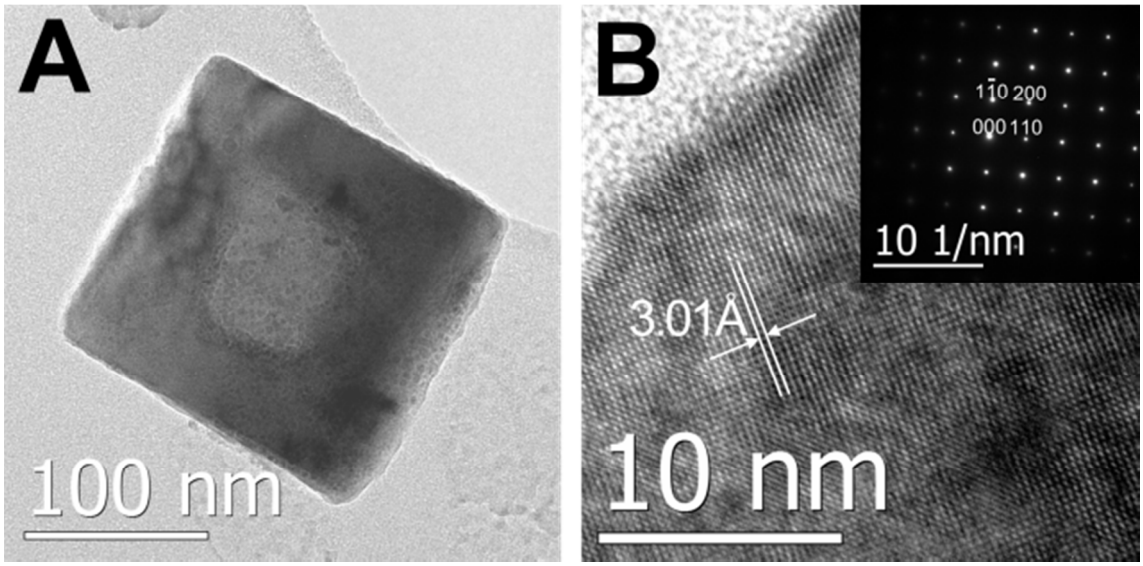

Figure S2. (A) TEM image of a typical crystalline Cu_2O nanocube from the Cu_2O sample electrodeposited on an ITO substrate by SWV. The SWV parameters used are t_0 = 2 s, f = 6 Hz, E_0 = -0.08 V, E_i = -0.08 V, E_f = -0.20 V, ΔE_{step} = -0.333 mV, E_{sw} = 80 mV, N = 5. (B) HRTEM lattice image near the edge of the Cu_2O nanocube shown in Graph A. The inset in (B) shows the SAED pattern in the same region.

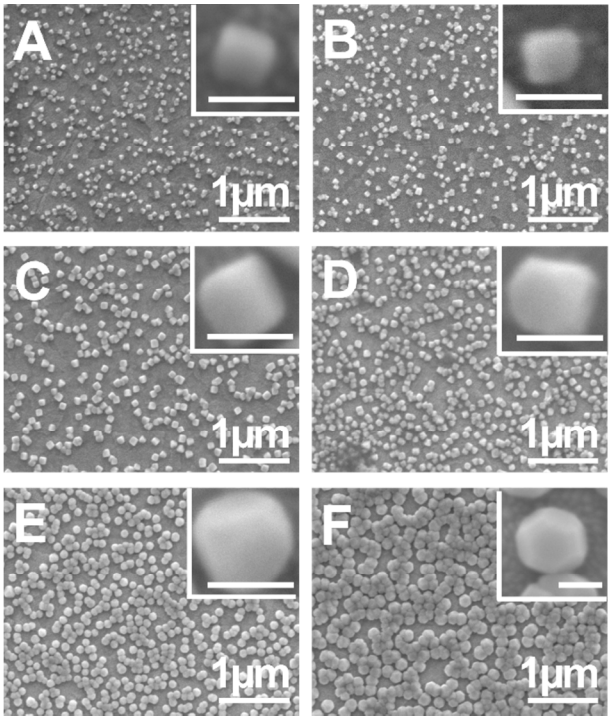

Figure S3. SEM images showing the effect of the deposition time (t) to the shape and size of the electrodeposited Cu_2O nanocrystals and their coalescence into a film by chronoamperometry (CA or simple $i \sim t$) method. The CA parameters used are t_0 = 2 s, E_0 = -0.2 V, E_i = -0.2 V. t =1 (A), 3 (B), 5 (C), 10 (D), 20 (E), and 40 min (F), respectively. The scale bars in the insets represent 100 nm.

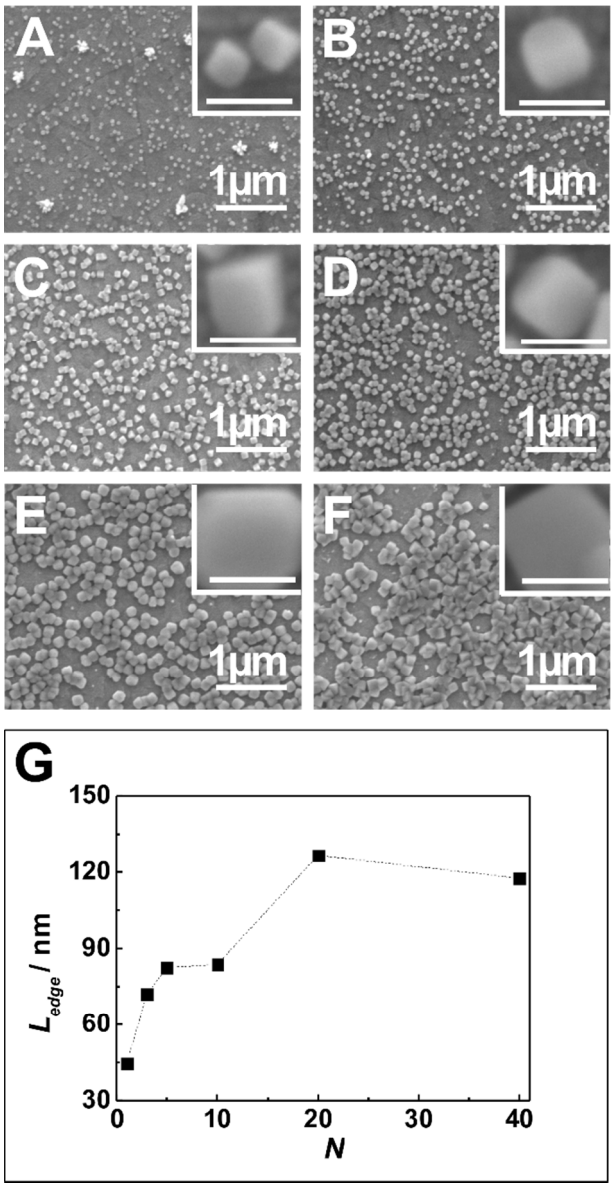

Figure S4. SEM images showing the effect of reversing the scan direction in SWV to the nucleation and the size of the electrodeposited Cu_2O nanocubes under the condition of $|\Delta E_{step}| << E_{sw}$ and $|\Delta E_{step}| << |E_f - E_i|$. The SWV parameters used are same as that of Figure-9, except that $E_0 = E_i = -0.20$ V and $E_f = -0.08$ V. N = 1 (A), 3 (B), 5 (C), 10 (D). 20 (E), and 40 (F), respectively. Graph-G shows the size variation of Cu_2O nanocubes when N was changed from 1 to 40. The scale bars in the insets represent 100 nm.

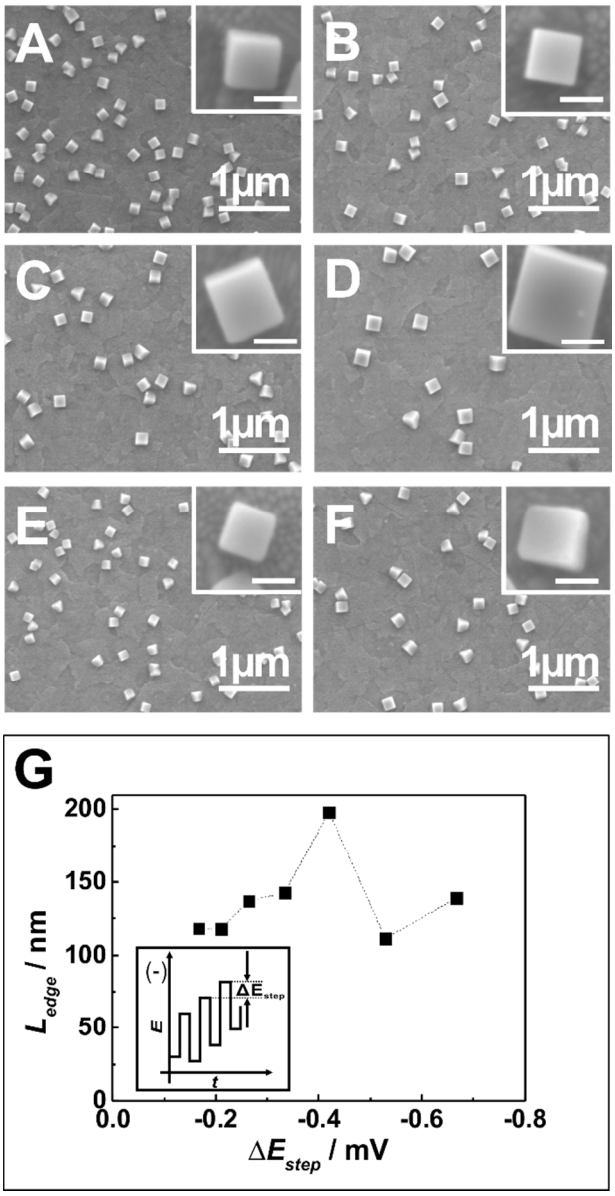

Figure S5. SEM images showing the effect of the step potential (ΔE_{step}) in SWV to the nucleation and the size of the electrodeposited Cu_2O nanocubes under the condition of $|\Delta E_{step}| << E_{sw}$ and $|\Delta E_{step}| << |E_f - F_i|$. ΔE_{step} = -0.167 (A), -0.210 (B), -0.264 (C), -0.420 (D), -0.529 (E), and -0.667 mV (F), respectively. Graph-G shows the size variation of Cu_2O nanocubes when ΔE_{step} was changed from -0.167 to -0.667 mV, corresponding to the change of the scan rate from 1 to 4 mV/s. Other SWV parameters are t_0 = 2 s, f = 6 Hz, E_0 = -0.08 V, E_i = -0.08 V, E_f = -0.20 V, E_{sw} = 80 mV, N = 1. The scale bars in the insets represent 100 nm.

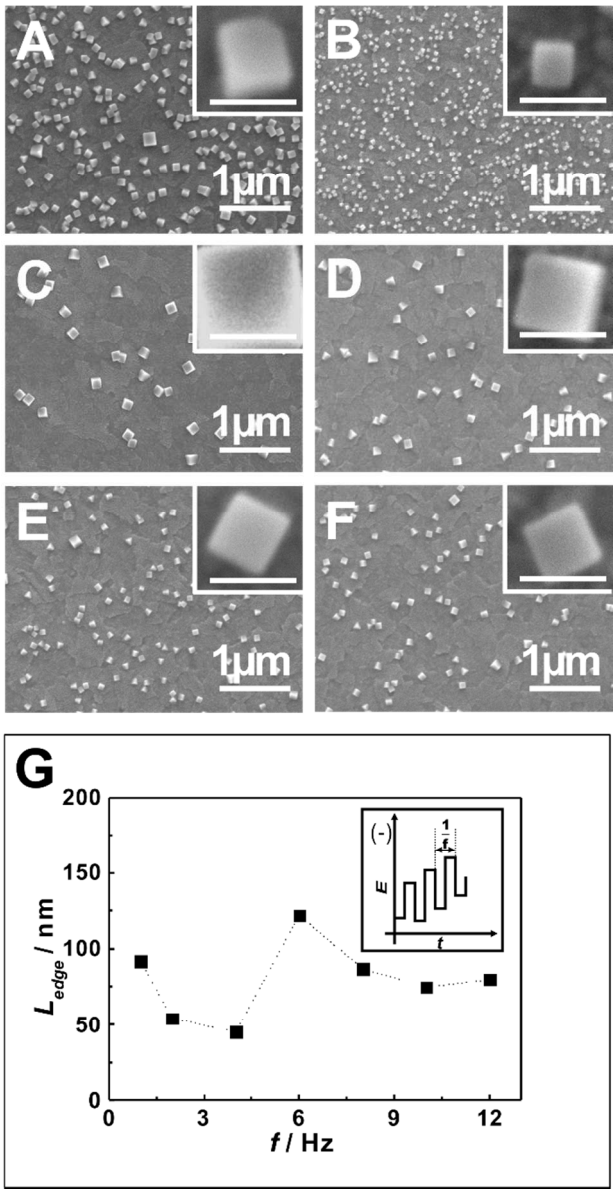

Figure S6. SEM images showing the effect of the frequency (f) in SWV to the size of the electrodeposited Cu_2O nanocubes under the condition of $|\Delta E_{step}| << E_{sw}$ and $|\Delta E_{step}| << |E_f - E_i|$. f = 1 (A), 4 (B), 6 (C), 8 (D), 10 (E) and 12 Hz (F), respectively. Graph-G shows the size variation of the deposited Cu_2O nanocubes when f is changed from 1 to 12 Hz. Other SWV parameters are t_0 = 2 s, E_0 = -0.08 V, E_i = -0.08 V, E_f = -0.20 V, ΔE_{step} = -0.333 mV, E_{sw} = 80 mV, N = 1. The scale bars in the insets represent 100 nm.

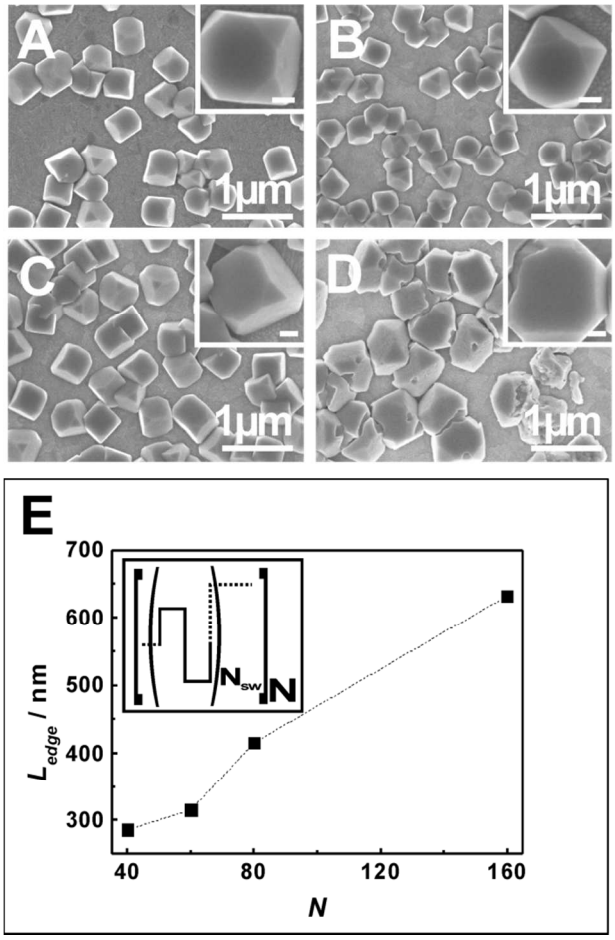

Figure S7. Same as Figure 9 except N = 40 (A), 60 (B), 80 (C), and 160 (D), respectively. Graph-E shows the size variation of the deposited Cu_2O nanocubes when N is changed from 40 to 160. With the increase of N, the shape of the electro-deposited Cu_2O particles deviates considerably from that of cube. The deposited Cu_2O particles eventually coalescence into a film with the cracks formed from the inter-particle boundaries. The scale bars in the insets represent 100 nm.

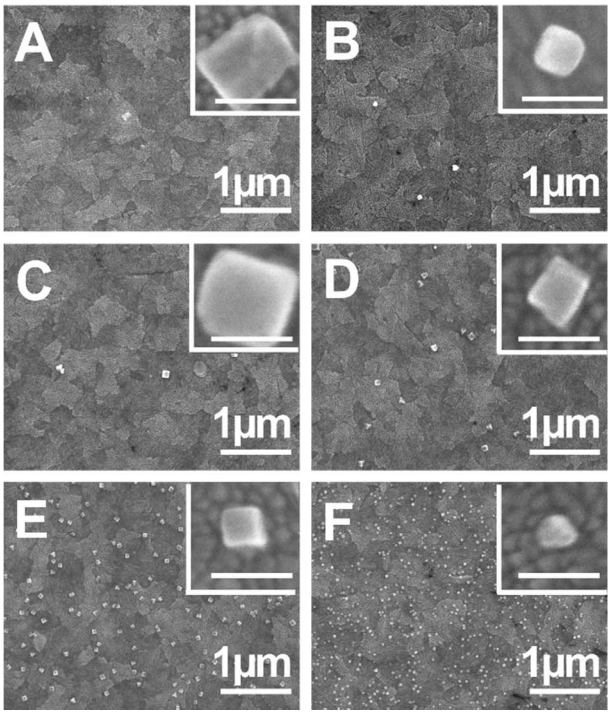

Figure S8. SEM images showing the effect of the set potential (E_0) to the seeding of Cu_2O before any SWV pulses were applied. E_0 (*vs.* SCE) = 0.04 (A), -0.02 (B), -0.06 (C), -0.10 (D), -0.14 (E), and -0.20 V (F), respectively. t_0 = 2 s. The scale bars in the insets represent 100 nm.

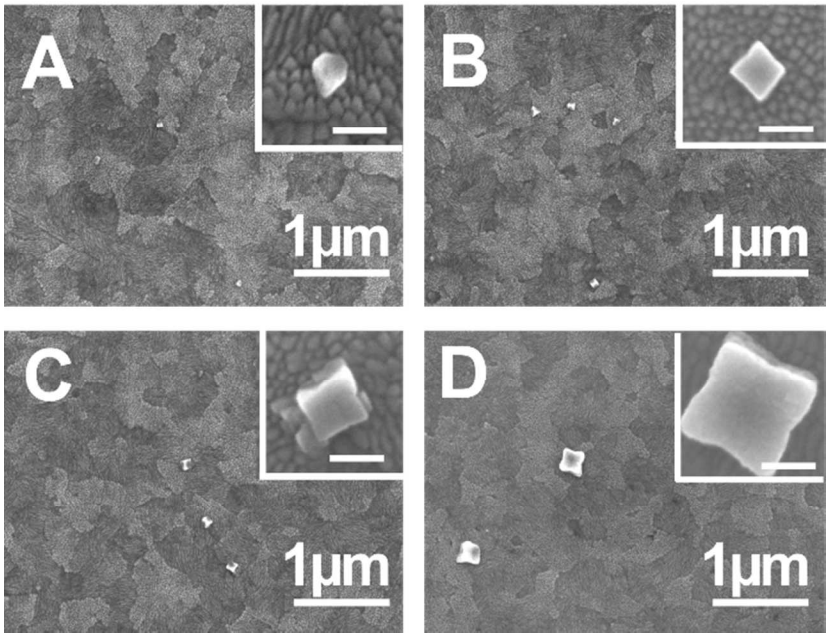

Figure S9. SEM images showing the effect of the waiting time (t_0) at E_0 to the seeding of Cu_2O before any SWV pulses were applied. t_0 = 1 (A), 2 (B), 3 (C), 5 s (D), respectively. E_0 = -0.08 V. The scale bars in the insets represent 100 nm.

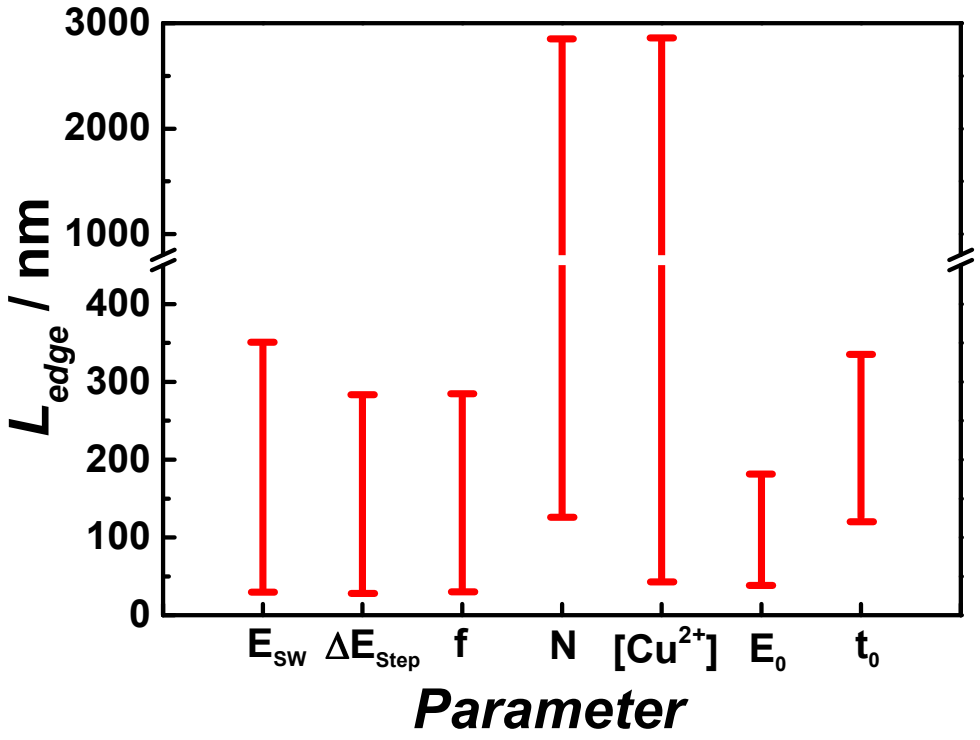

Figure S10. Graph illustrating the shape-invariant size-tunable ranges of the electrodeposited Cu_2O nanocubes by adjusting individual parameters in SWV examined in this study. The data were from Figure-5 for E_{sw}, Figure 11-A for ΔE_{step}, Figure 11-B for f, Figure 11-D for N, Figures 10 and 11-D for $[Cu^{2+}]$, Figure 14 for E_0, and Figure 15 for t_0, respectively.

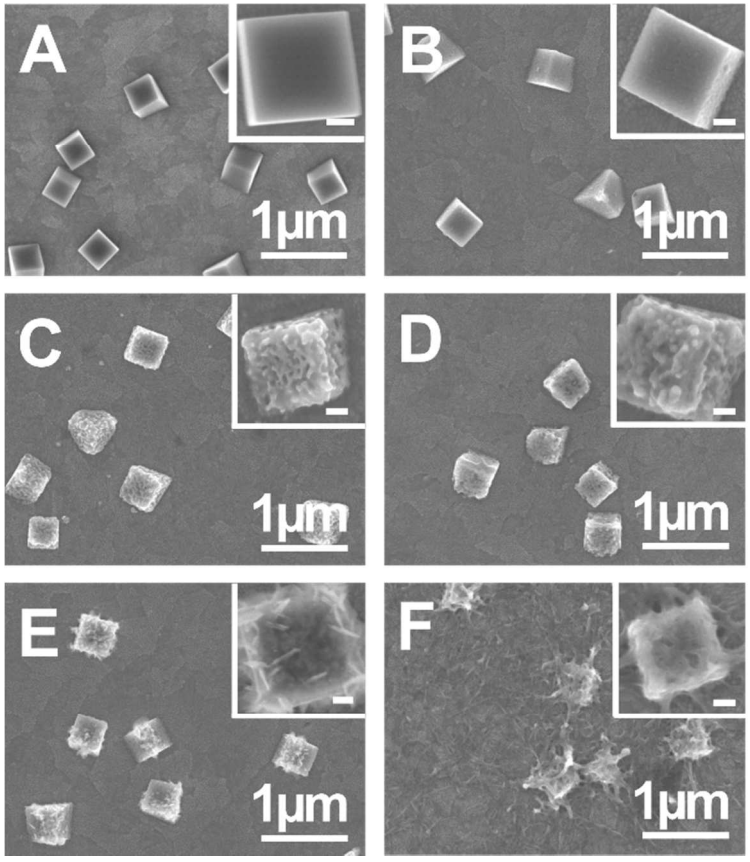

Figure S11. SEM images showing the effect of the time used in the galvanic displacement reaction to the structure of the fabricated Cu_2O@Ag composites. The reaction time is 0 (A), 0.5 (B), 1 (C), 2 (D), 3 (E) and 4 hours (F), respectively, in 1 mM $AgNO_3$ aqueous solution at ambient condition in the dark without any supporting electrolyte. The cubic Cu_2O templates were fabricated by SWV using the same parameters as that of Graph-E in Figure-10. The scale bars in the insets represent 100 nm.

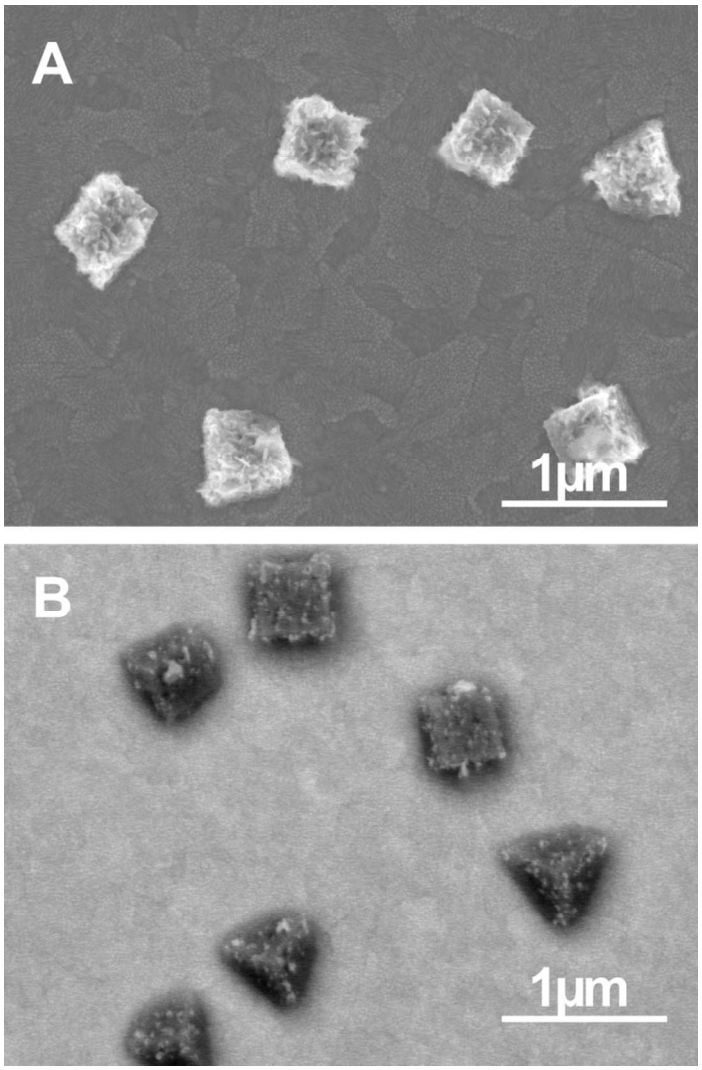

Figure S12. SEM images of the Cu_2O@Ag composites taken by the secondary electron mode (SEI, **A**) and the backscattered electron mode (BEI, **B**) to examine the morphology and the composition of the as-fabricated Cu_2O@Ag, respectively. The Cu_2O@Ag sample was fabricated using the same conditions as that for Graph E, Figure-S11.

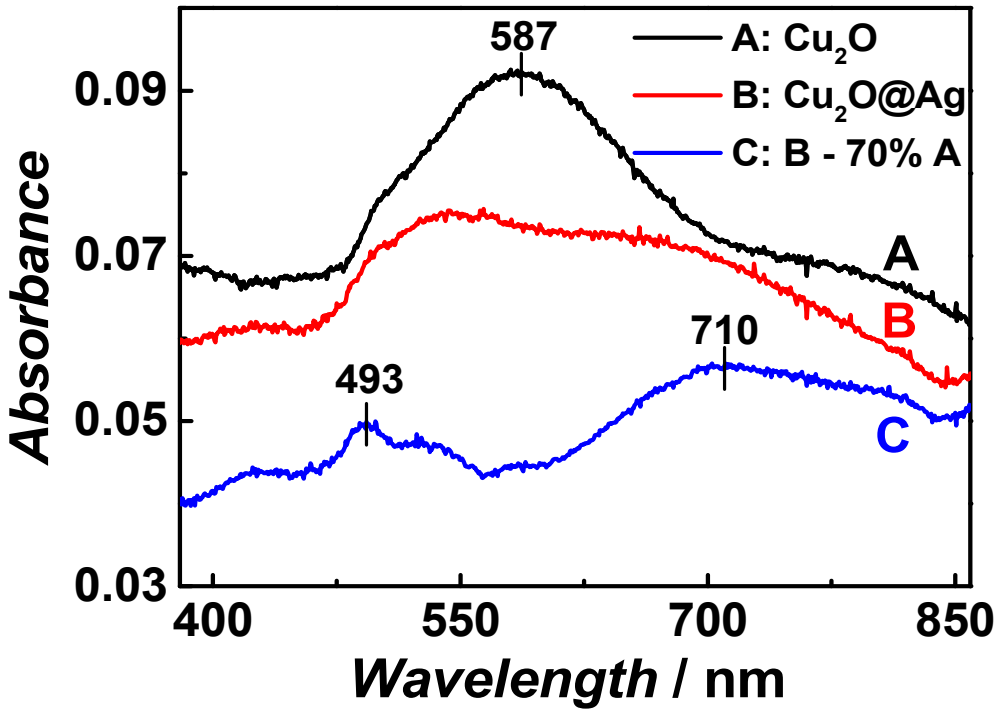

Figure S13. UV-Vis-NIR spectra of the Cu_2O cubic nano-templates (A), Cu_2O@Ag composites (B), and the estimated contribution from the Ag shell (C = B - 70%A). The Cu_2O and Cu_2O@Ag samples were fabricated using the same parameters as that for Graph E, Figure-S11.