

Electronic Supplementary Information

Table S1. Experimental conditions of Cu₂O geometrical particles synthesis.

Cu ₂ O particle	Initial temperature	C.A.	Anion	Medium	Aging temperature
O-Cu ₂ O	R.T.	-	Chloride	H ₂ O	70
TO PVP-Cu ₂ O	70	PVP	Chloride	H ₂ O	70
TO-Cu ₂ O	R.T.	-	Acetate	H ₂ O	70
C-Cu ₂ O	70	-	Chloride	H ₂ O	70
S-Cu ₂ O	R.T.	-	Chloride	50% EtOH	80

R.T. = room temperature, C.A. = capping agent

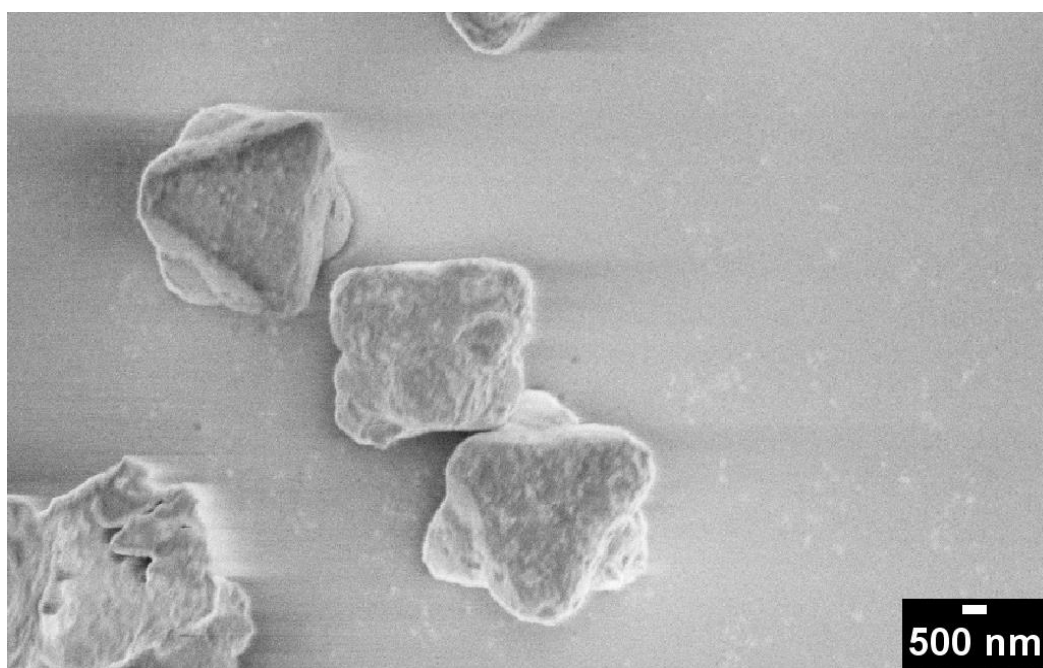


Figure S1. SEM image of Cu₂O star-like particles synthesized at 70°C.

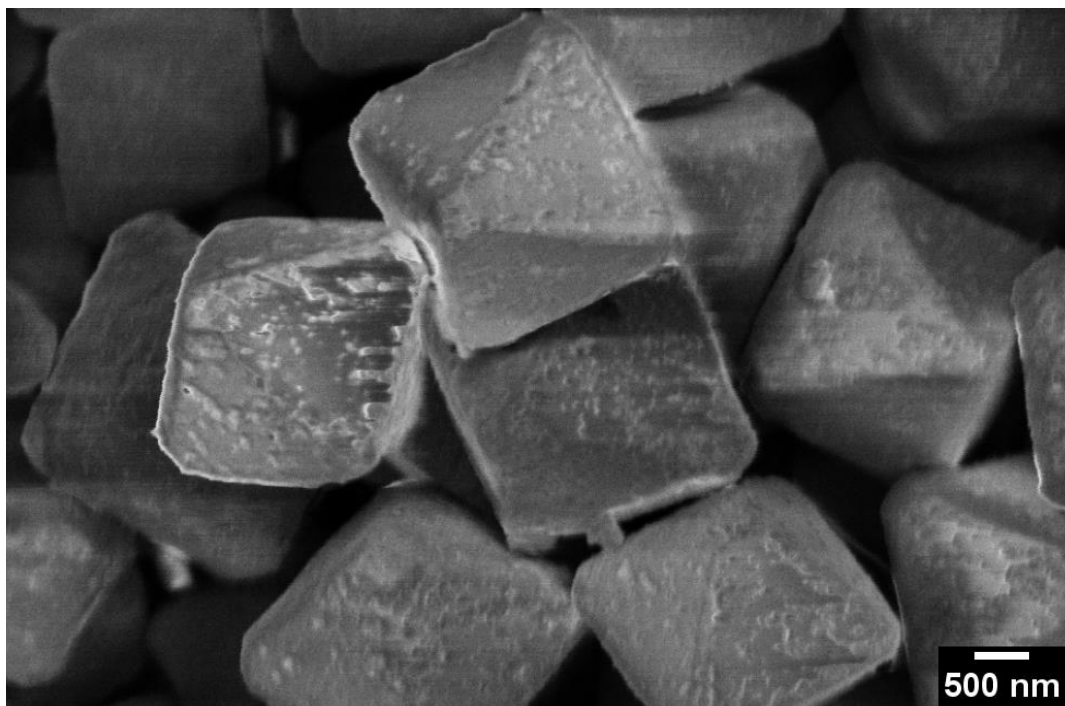


Figure S2. SEM image of Cu₂O star-like particles synthesized with at 70°C as an initial temperature reaction.

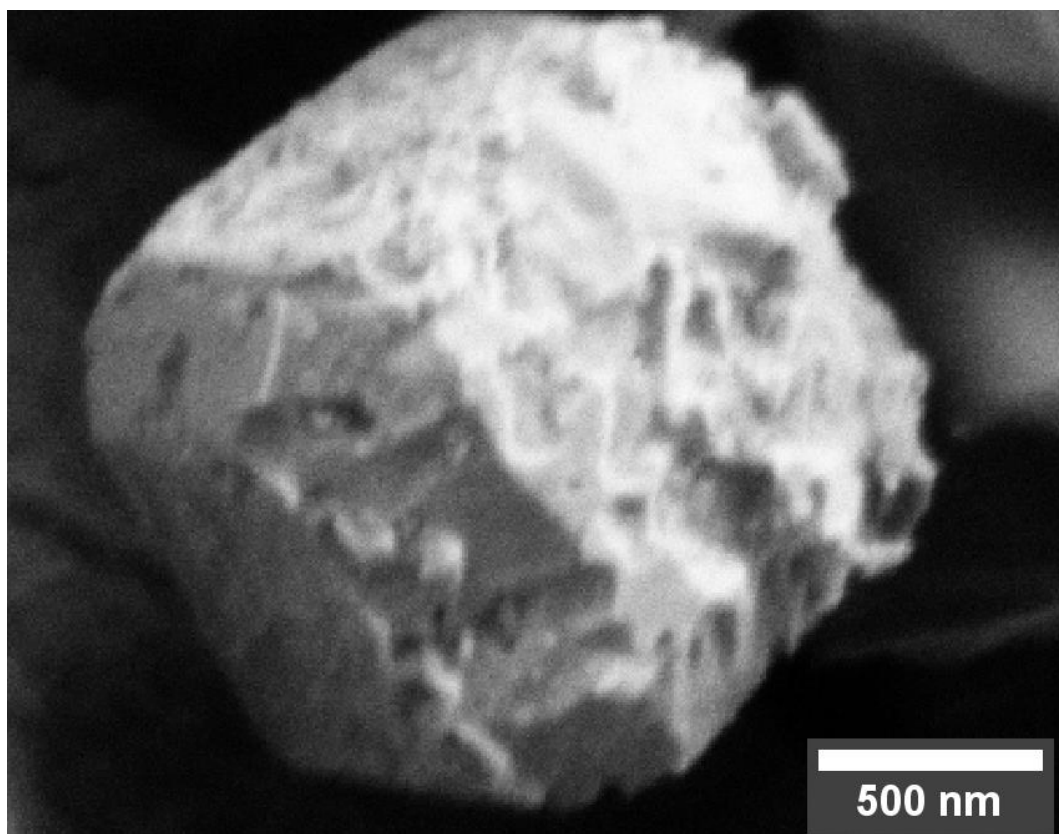


Figure S3. SEM image of TO PVP-G aerogel with no O₂ on the reaction solution.

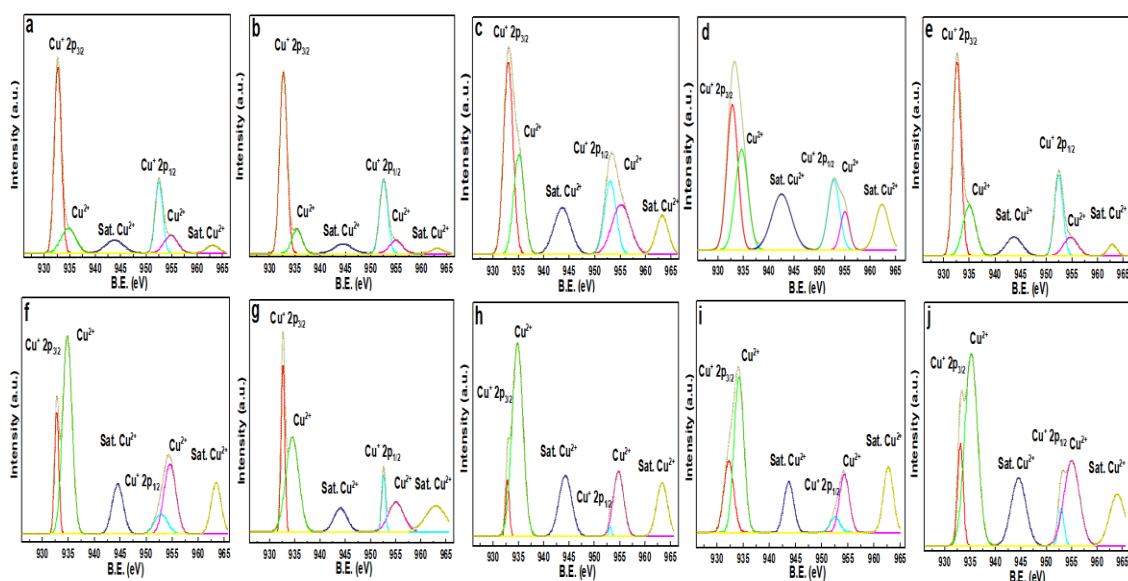


Figure S4. Cu_{2p} XPS spectra of geometrical Cu₂O particles: (a) O-Cu₂O, (b) TO-Cu₂O, (c) TO PVP-Cu₂O, (d) C-Cu₂O and (e) S-Cu₂O and Cu₂O@aerogels: (f) O-G, (g) TO-G, (h) TO PVP-G, (i) C-G and (j) S-G.

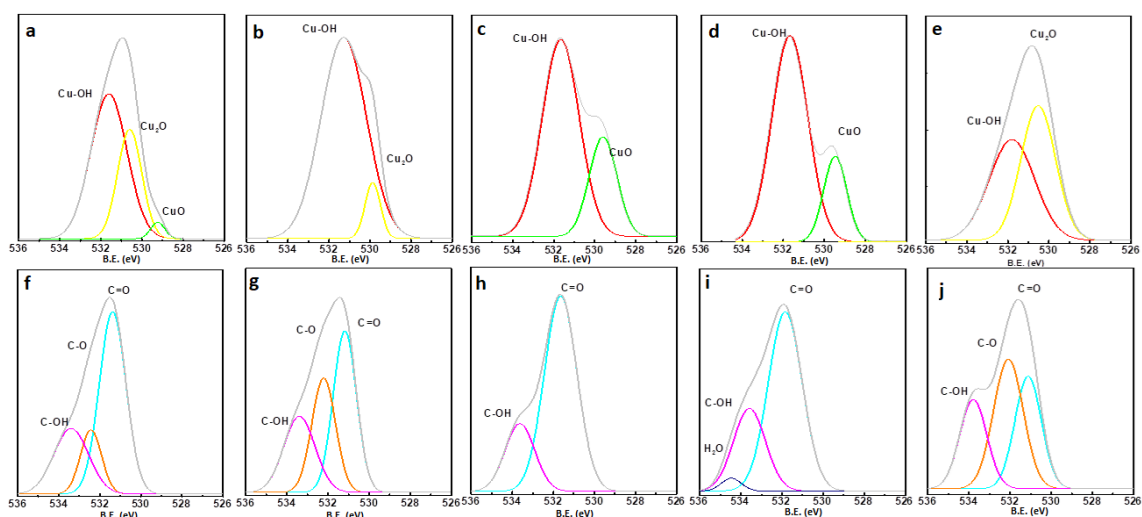


Figure S5. O_{1s} XPS spectra of geometrical Cu₂O particles: (a) O-Cu₂O, (b) TO-Cu₂O, (c) TO PVP-Cu₂O, (d) C-Cu₂O and (e) S-Cu₂O and Cu₂O@aerogels: (f) O-G, (g) TO-G, (h) TO PVP-G, (i) C-G and (j) S-G.

Table S2. Intensity of $\text{Cu}^+/\text{Cu}^{2+}$ ratio of Cu_2O particles and $\text{Cu}_2\text{O}@r\text{GO}$ aerogels and bandgap of geometrical Cu_2O particles.

Geometrical shape	Ratio $\text{Cu}^+/\text{Cu}^{2+}$		band gap (eV)
	Cu_2O	$\text{Cu}_2\text{O}@r\text{GO}$	
O- Cu_2O	2.31	0.41	2.00
TO PVP- Cu_2O	1.69	0.10	1.96
TO- Cu_2O	5.15	0.50	1.97
C- Cu_2O	1.26	0.46	1.99
S- Cu_2O	2.41	0.23	1.95

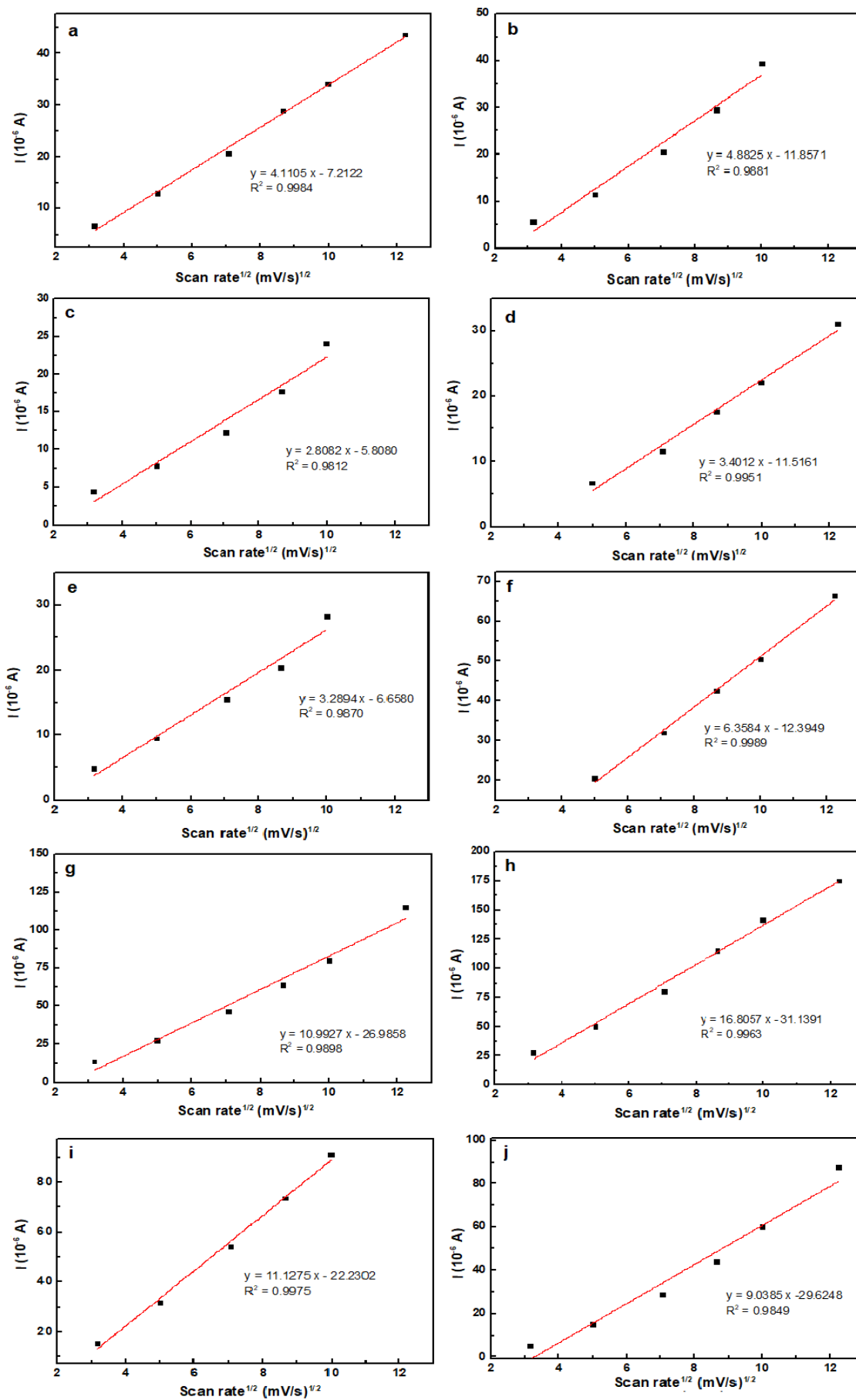


Figure S6. Oxidation current response versus square root of scan rate 10-150 mV/s of Cu₂O Particles (a) O-Cu₂O, (b) TO PVP-Cu₂O, (c) TO-Cu₂O, (d) C-Cu₂O, (e) S-Cu₂O and Cu₂O@rGO aerogel (f) O-G, (g) TO PVP-G, (h) TO-G, (i) C-G, (j) S-G.

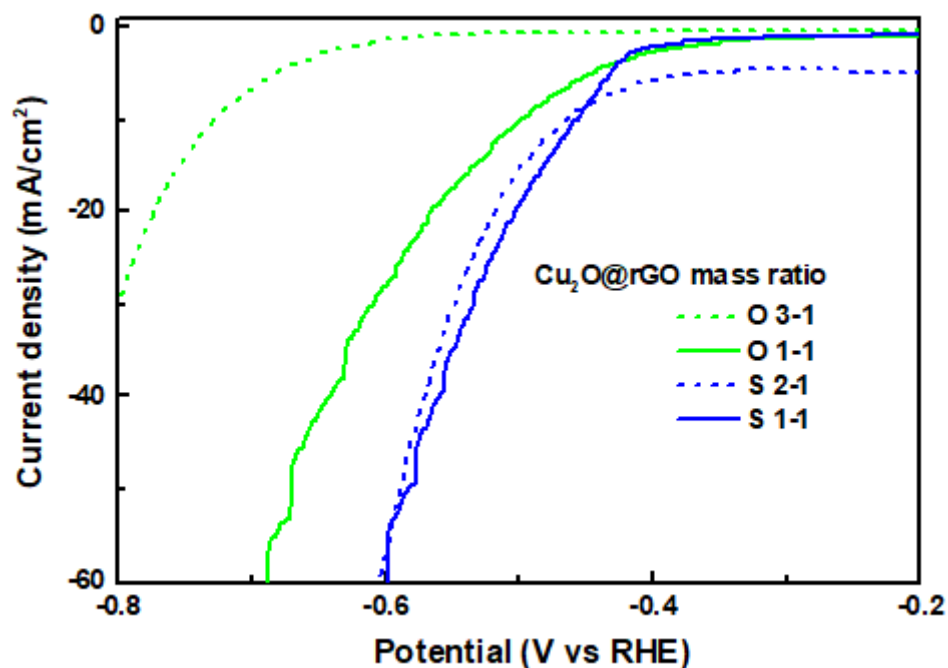


Figure S7. HER performance of mass ratio effect in Cu₂O@rGO aerogel. Linear Sweep voltammetry curves in 1N H₂SO₄ solution at scan rate 5 mV s⁻¹.

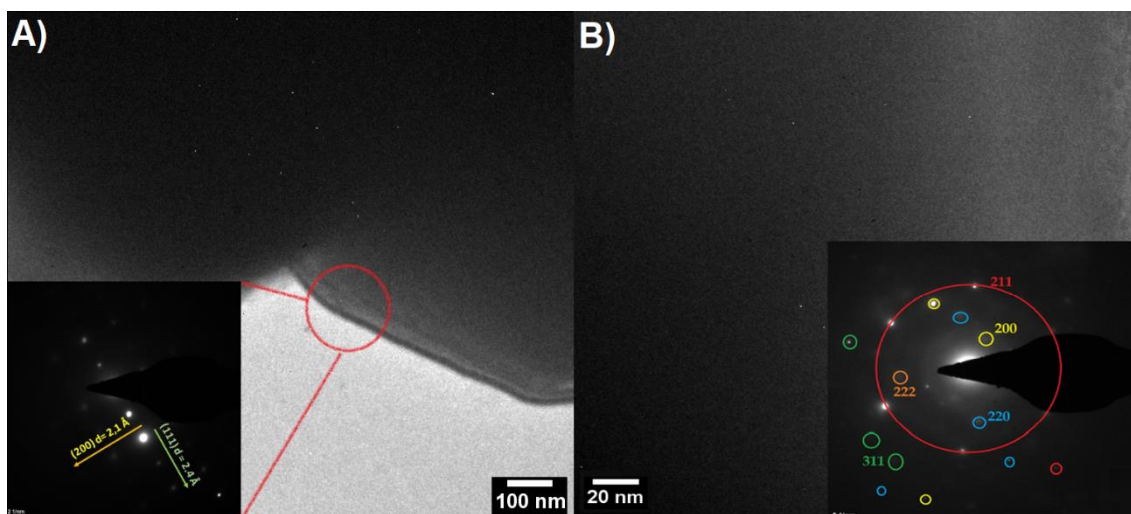


Figure S8. SAED-TEM images of Cu₂O star-like shape. (A) High magnification of electron diffraction on the (A) edges, (B) core of the particle.

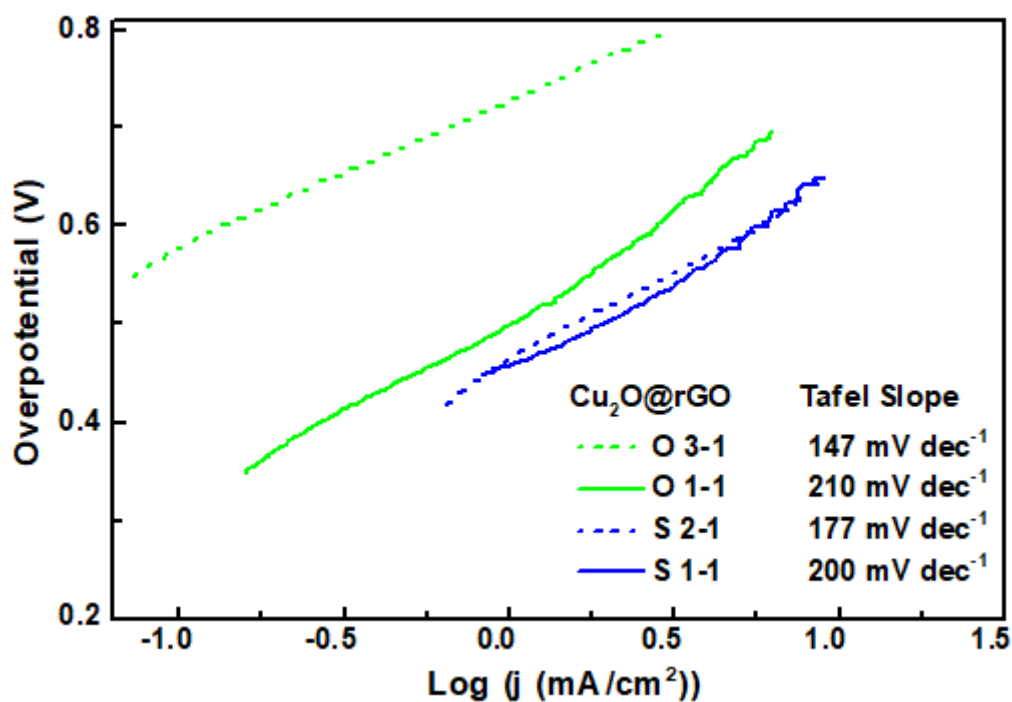


Figure S9. HER performance of mass ratio effect in $\text{Cu}_2\text{O@rGO}$ aerogel. Tafel plots of HER.

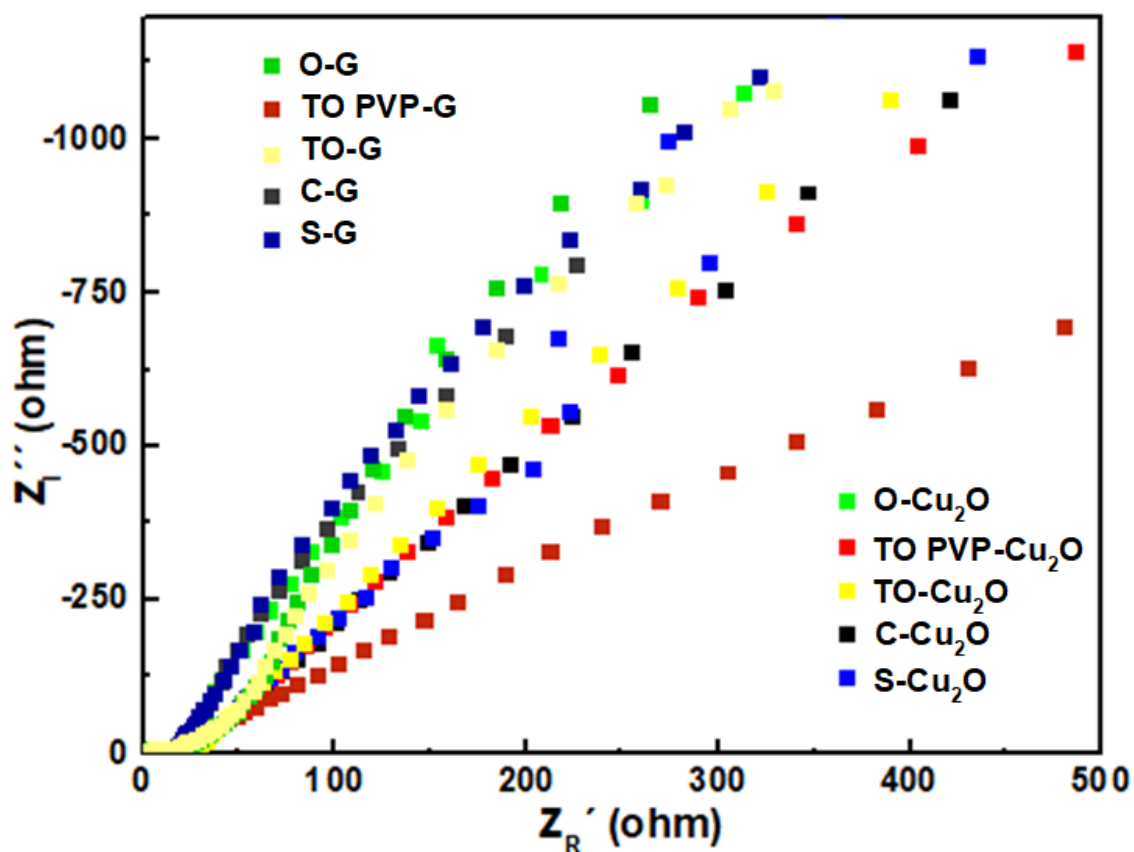


Figure S10. Nyquist plot of Cu_2O particles and $\text{Cu}_2\text{O@rGO}$ aerogel at 0 V vs RHE.

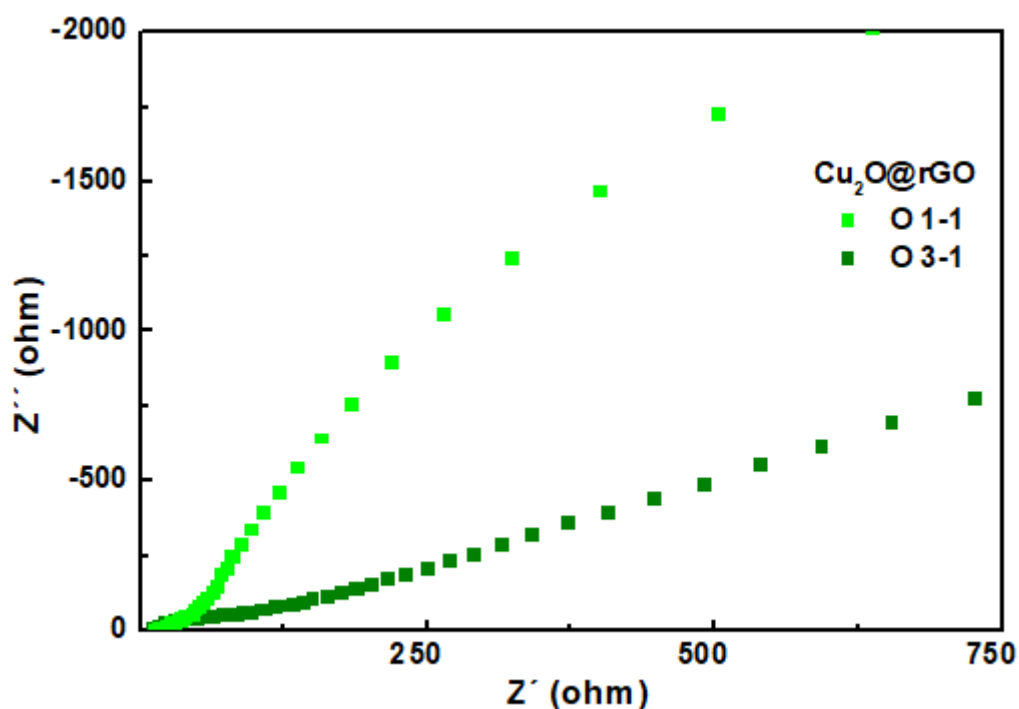


Figure S11. Nyquist plot of $\text{Cu}_2\text{O@rGO}$ aerogel mass ratio effect.

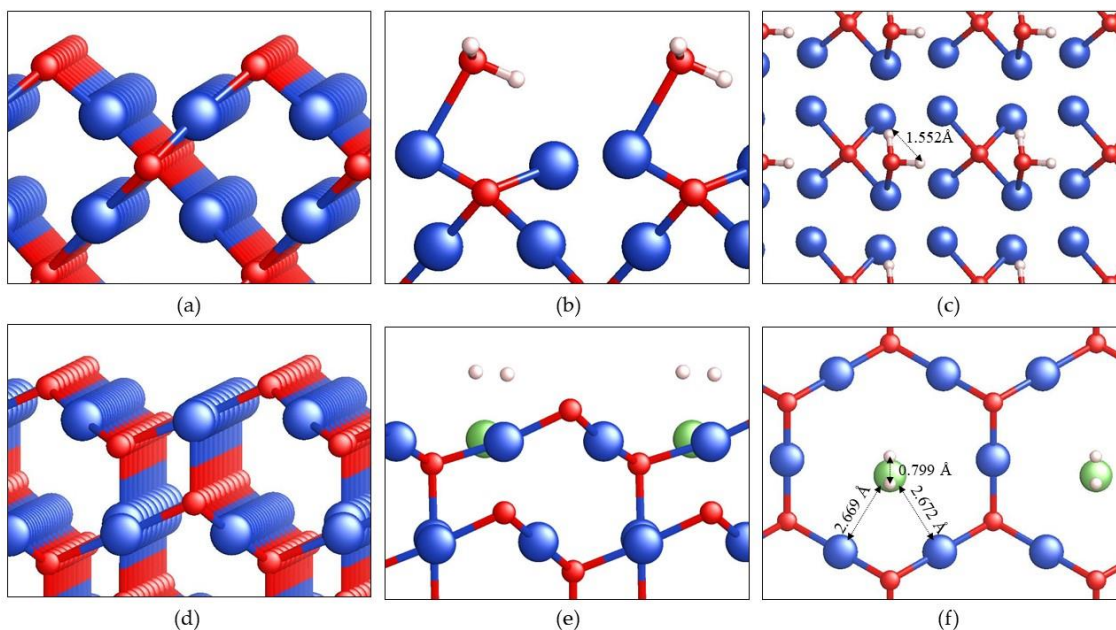


Figure S12. Most-favored configuration and energy of hydrogen adsorption on Cu_2O (111) and (100) surface: (a) pristine Cu_2O (100) surface, (b) side view, and (c) top view of H_2 adsorption on (100) surface; (d) pristine Cu_2O (111) surface, (e) side view, and (f) top view of H_2 adsorption on (111) surface. Cu-Cu and H-H bond lengths are labeled in (c) & (f) (All Cu atoms are in blue balls, except the coordinatively unsaturated Cu atoms are in green balls, O atoms are in red balls, and H atoms are in white balls. Bottom layers in (c) & (f) have been emitted for better view).