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Supporting Information

Silver-Copper Metallic Glass Electrocatalyst with High Activity and Stability Comparable to Pt/C for Zinc–Air Batteries

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Part 1. TEM results of AgCu-MG catalyst

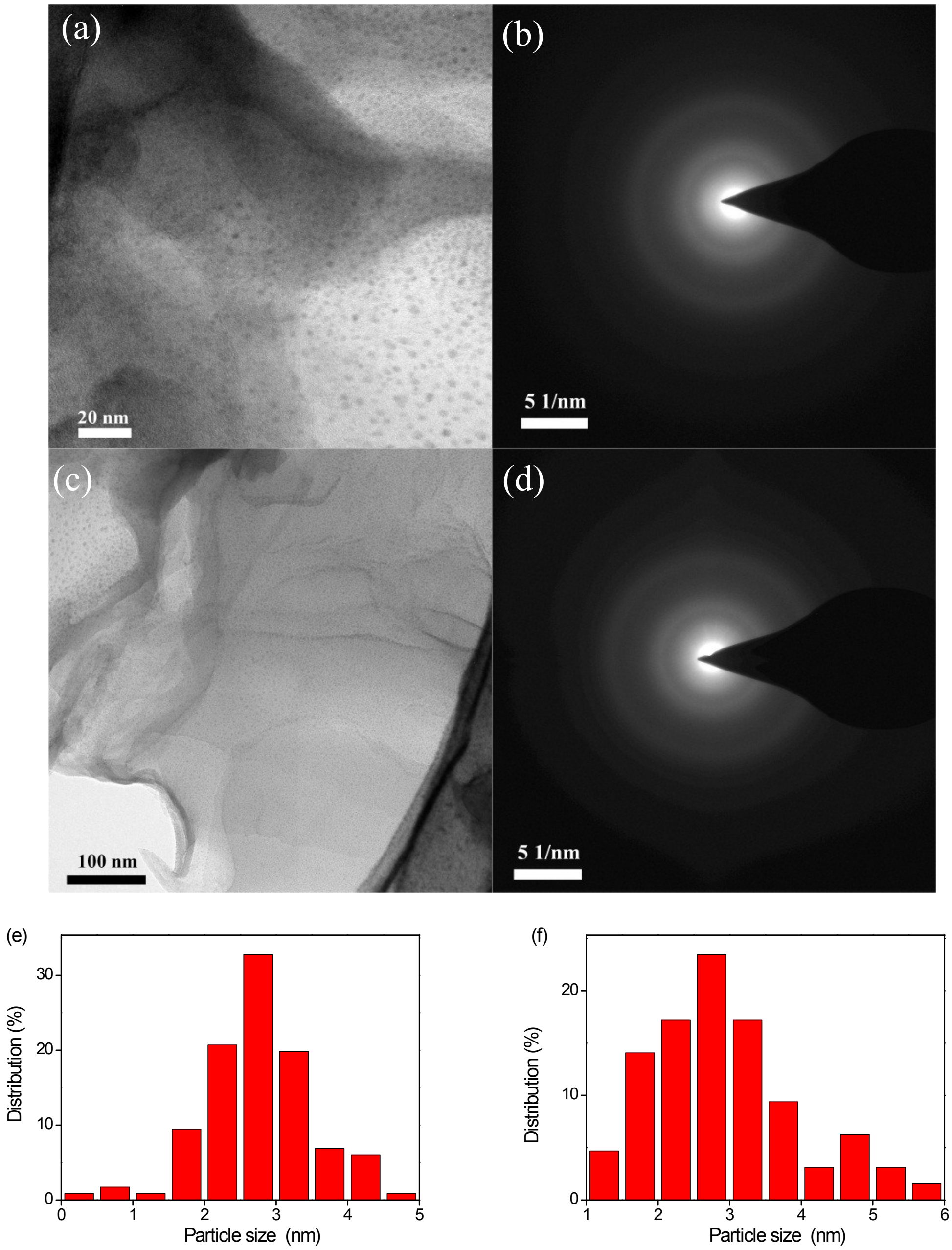

Figure S1. (a-d) TEM images, selected area diffraction patterns and, (e-f) particle size distribution of the AgCu-MG.

Part 2. The method of preparation of XRD patterns and the results of AgCu-MG catalyst

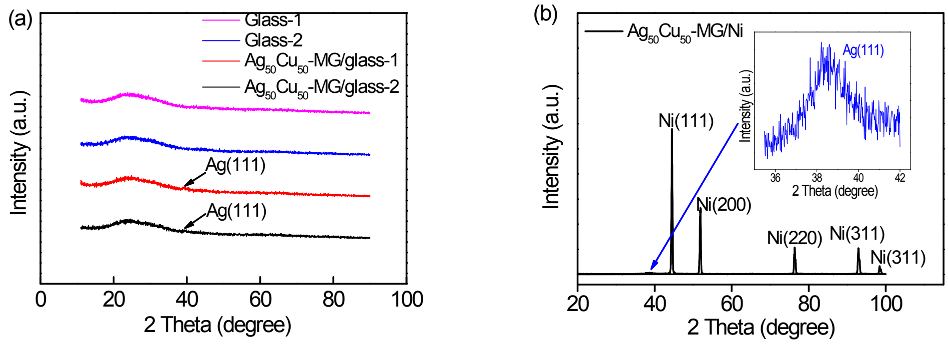

Figure S2. (a) Comparative X-ray diffraction of glass and AgCu-MG on a plain glass, (b) X-ray diffraction of AgCu-MG on nickel foam.

Part 3. The SEM patterns and the Elements mapping of the AgCu-MG catalyst

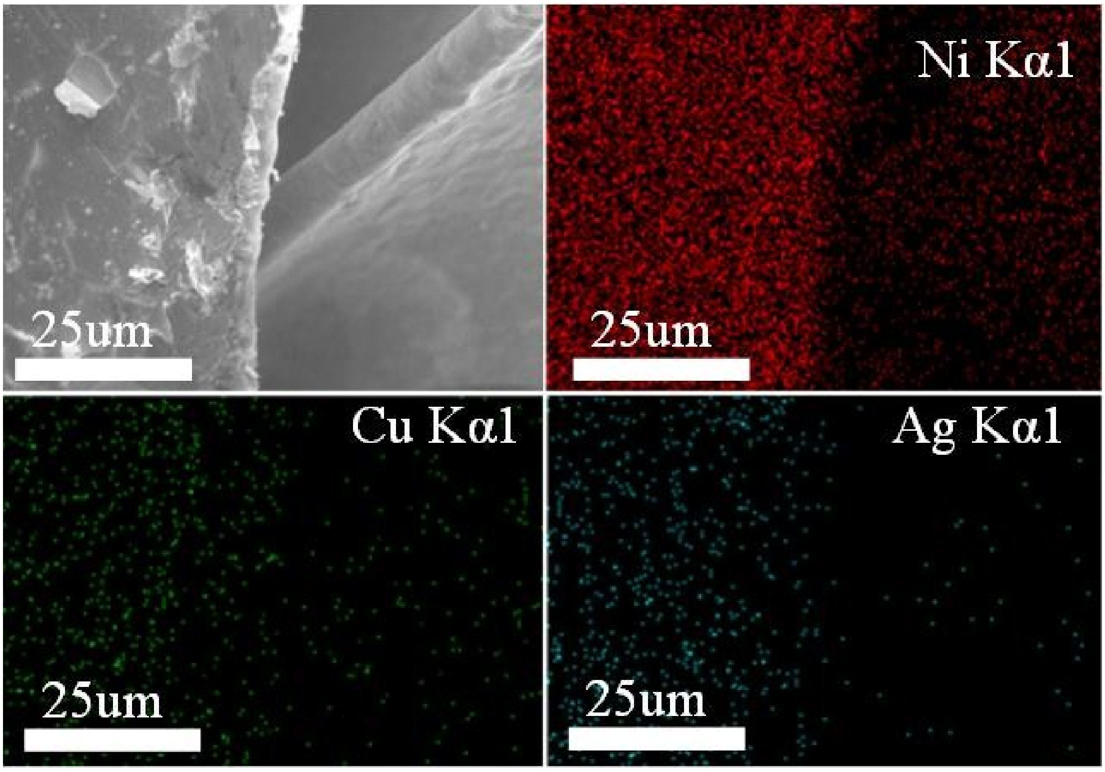

Figure S3. Elements mapping and the SEM image of the AgCu-MG on nickel foam.

Part 4. Kinetic of oxygen reduction

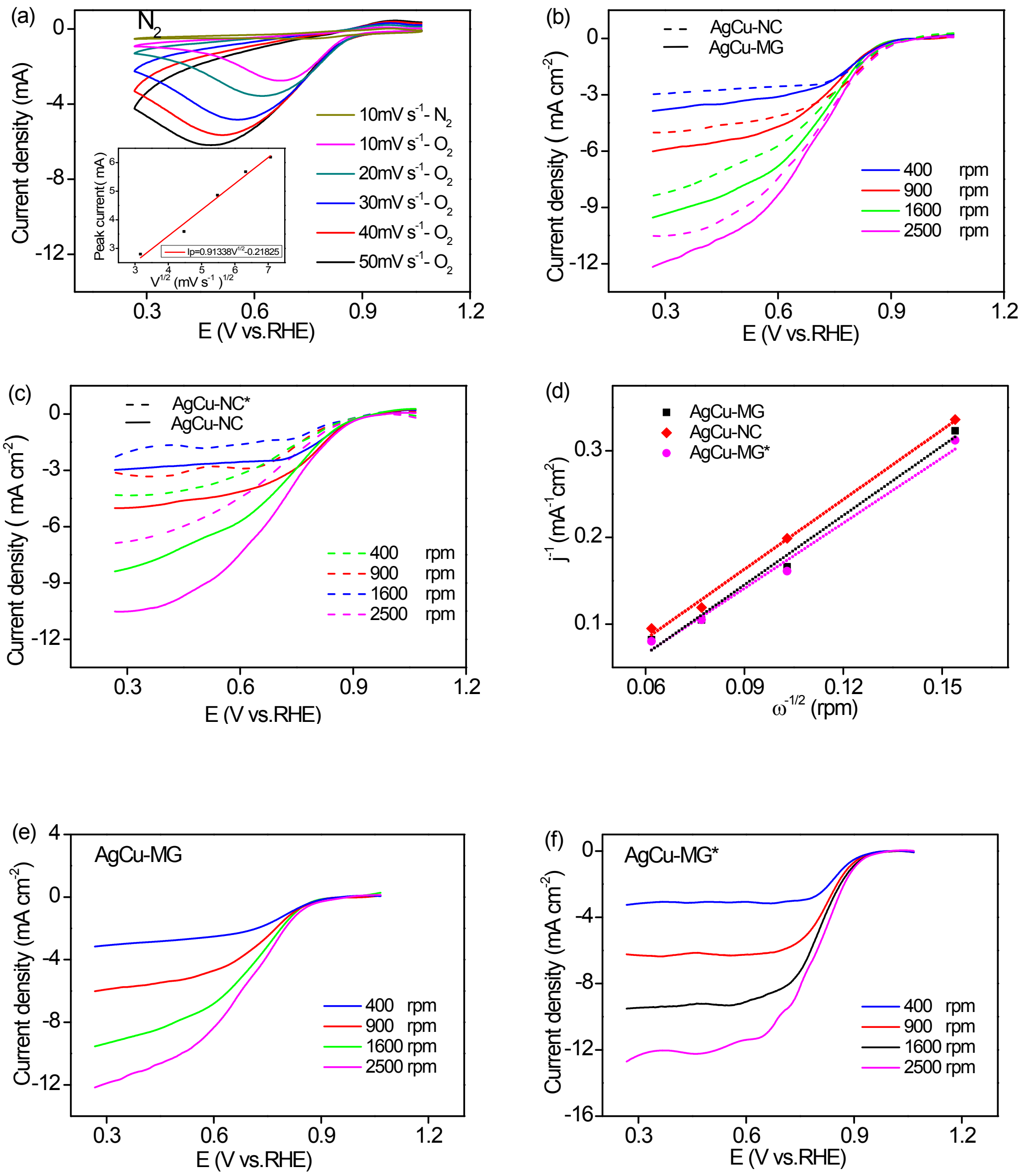

Figure S4. (a) The CV curves of the AgCu-MG catalyst in N_2 and O_2 saturated solution, (b) ORR polarization curves of the AgCu-MG, dash lines present the corresponding patterns AgCu-NC (AgCu nanocrstalline catalyst), (c) ORR polarization curves of the AgCu-NC, dash lines present the corresponding patterns after 1000 CV cycles, (d) The Koutecky-Levich plots at the limiting current of the AgCu-MG, AgCu-NC and AgCu-MG* catalysts, (e) ORR polarization curves of AgCu-MG in various rotation speeds, (f) ORR polarization curves of AgCu-MG* in various rotation speeds.

The reduction of O_2 in alkaline electrolytes can proceed through one of two pathways. The first pathway is O_2 directly reduction to OH^- ions, which is called the four-electron pathway, as equation 1, and the second pathway is O_2 reduction to HO_2^- ions as equation 2 and subsequent reduction of peroxide ion to OH^- as equation 3 or decomposition of peroxide ion as equation 4, which is called two-electron pathway:

$$O_2+2H_2O+4e^-\rightarrow 4OH^- \quad (1)$$

$$O_2+H_2O+2e^-\rightarrow HO_2^-+OH^- \quad (2)$$

$$HO_2^-+H_2O+2e^-\rightarrow 3OH^- \quad (3)$$

$$2HO_2^-\rightarrow 2OH^-+O_2+2e^- \quad (4)$$

According to the Koutecky-Levich equations, the number (n) of electrons transferred in the ORR process can be obtained from the RDE results. The Koutecky-Levich equations are as following:

$$j^{-1}=j_k^{-1}+(0.62nFC_0D^{2/3}v^{-1/6}\omega^{1/2})^{-1} \quad (5)$$

$$j_k^{-1}=(nFAKTC_0)^{-1} \quad (6)$$

Where j is the measured electrode current density, j_k is the kinetic current density, and ω is the electrode rotation rate. The value of D is 1.9×10^{-5} cm^2/s, C_0 is 1.2×10^{-3} mol/L, ν is 1.1×10^{-2} cm^2/s, and F is 96485 C/mol, A is the is the electrode area, *K* is the kinetic rate constant for catalytic reaction, T is the quantity of catalyst on the surface of the electrode.

Part 5. XPS results of AgCu-alloy patterns

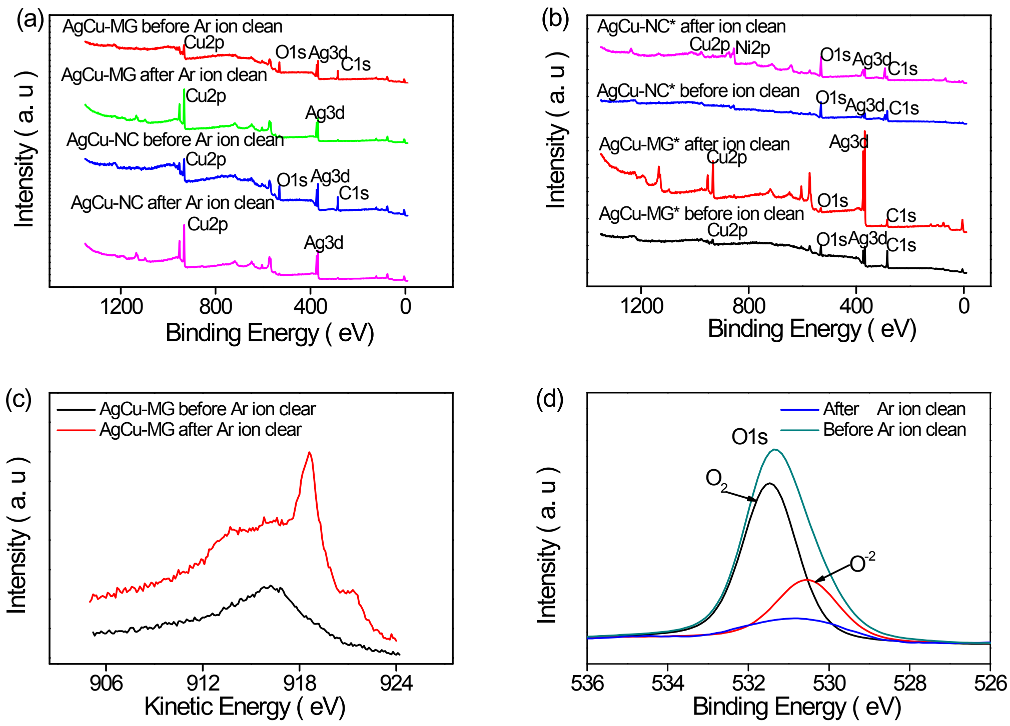

Figure S5. (a) Full survey scan XPS before and after Ar ion etching for the AgCu-MG and AgCu-NC samples,(b) for the AgCu-MG* and AgCu-NC* (c) Auger lines (AES) of Cu in AgCu-MG before and after ion clean.(d) O_{1s} regions in AgCu-MG before and after ion clean.

Part 6. Schematic of AuCu-MG-based air electrode and rechargeable zinc-air battery

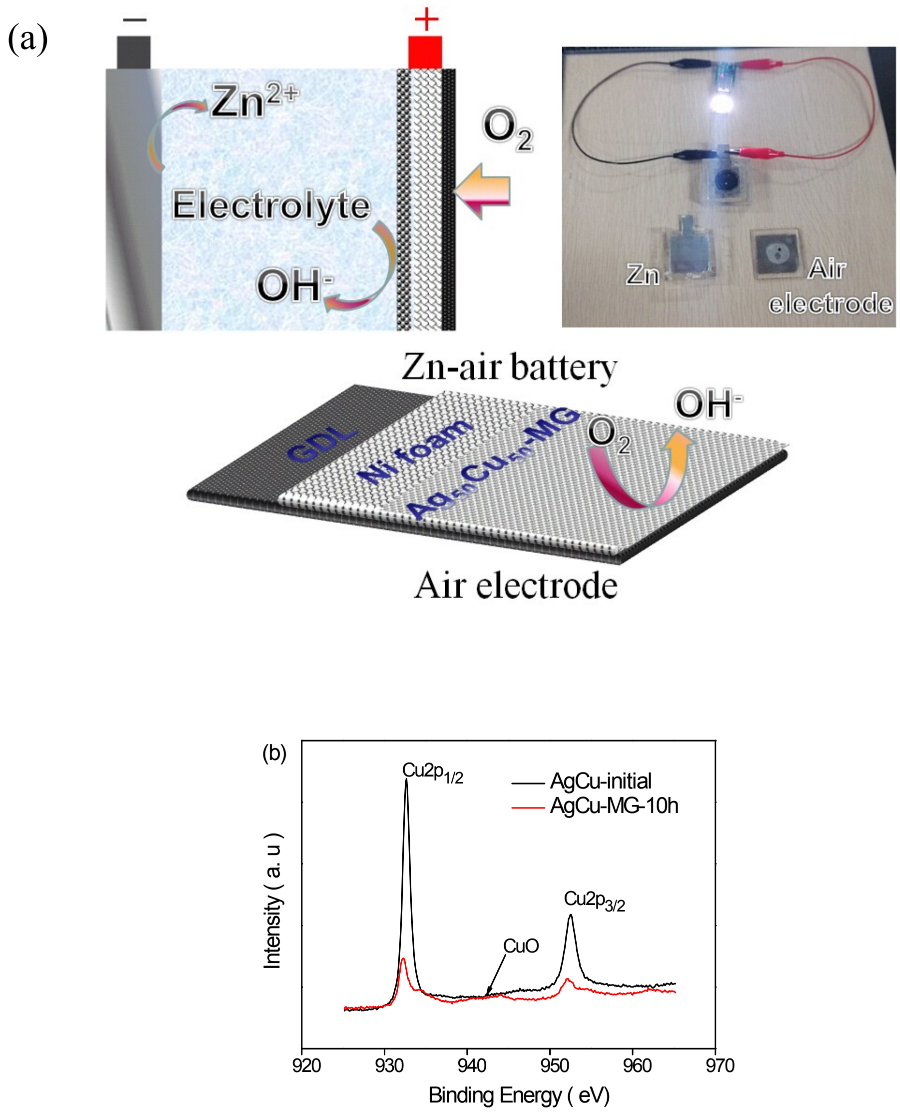

Figure S6. (a) Schematic of air electrode and a zinc-air battery, and a digital photograph of LED lights powered by the zinc-air battery systems, (b) XPS analysis of AgCu-MG after discharge for 10 hours in Zn-air battery.

(I) For primary Zn-air system, we choose 6M KOH solution as electrolyte, electrochemical reactions that occur in primary Zn-air system as follows:

(1) Discharge

Zinc plate (negative electrode):

$Zn + 4OH^{-} = Zn(OH)2- 4 + 2e$

Zn(OH)2- 4 = ZnO + H_2O + 2OH^-

Air electrode (positive electrode):

1/2O_2+ H_2O + 2e = 2OH^-

Overall reaction: 2Zn + O_2=2ZnO

(II) For primary Zn-air system, we choose 6M KOH +0.1M Zn(CH_3COO)$_2$ solution as electrolyte, electrochemical reactions that occur in primary Zn-air system as follows:

(1) Discharge

Zinc plate (negative electrode):

Zn + 4OH^-= Zn(OH)2- 4 + 2e

Zn(OH)2- 4 = ZnO + H_2O + 2OH^-

Air electrode (positive electrode):

1/2O_2+ H_2O + 2e = 2OH^-

Overall reaction: 2Zn + O_2=2ZnO

(2) Charge

Zinc plate (cathode):

ZnO + H2O + 2OH= Zn(OH)2- 4

Zn(OH)2- 4 + 2e = Zn + 4OH^-

Air electrode (anode):

2OH^- =1/2O_2+ H_2O + 2e

Overall reaction:

2ZnO = 2Zn + O_2

Part 7. A long-term discharge–charge cycling of two-electrode chargeable zinc–air batteries based on AgCu-MG catalysts

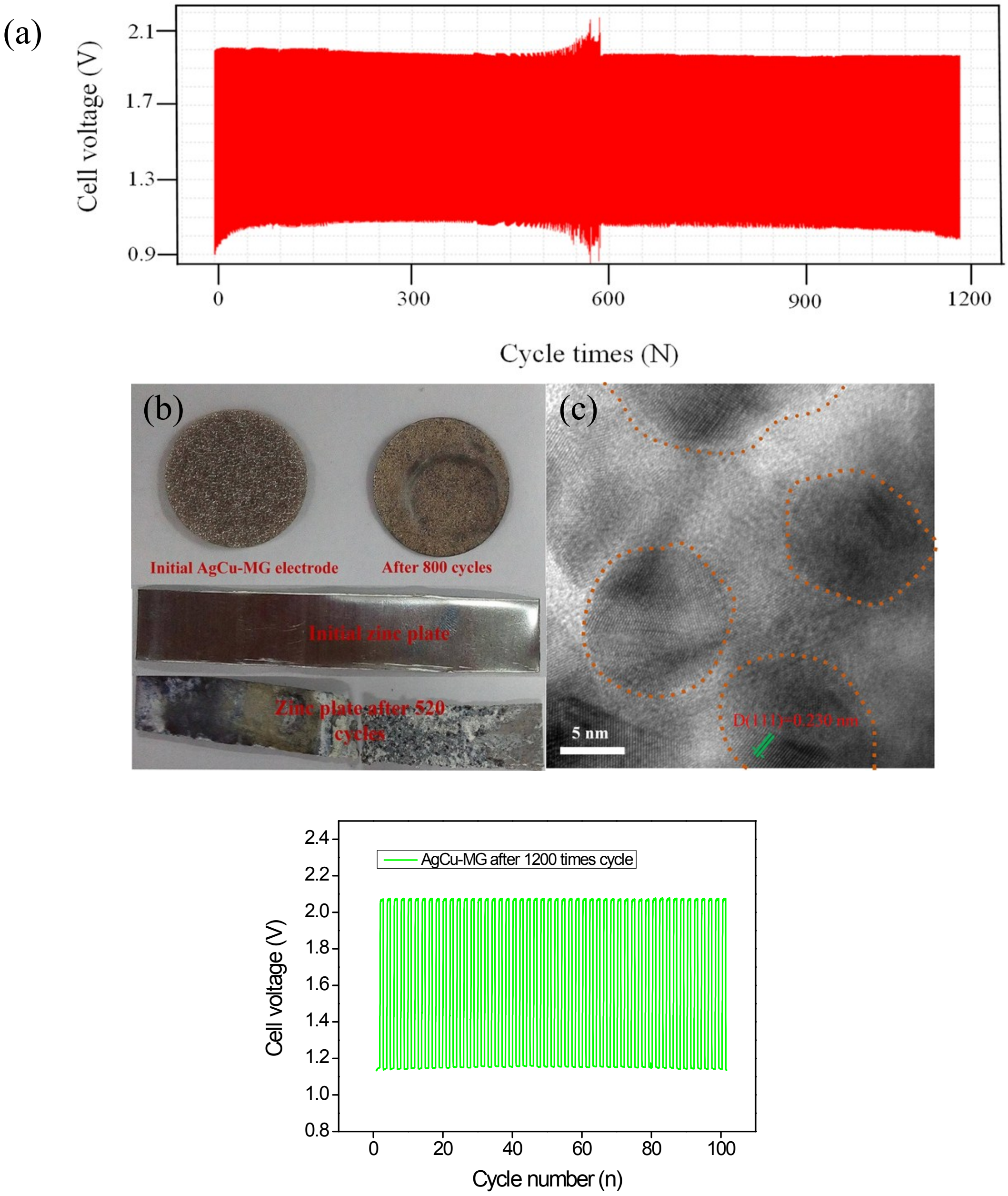

Figure S7. (a) A discharge–charge cycling of two-electrode rechargeable zinc–air batteries based on AgCu-MG catalysts for more than 1000 times when only air is uesd for test, (b) Images of AgCu-MG catalysts on nickel foam before and after 1000 cycles, and images of the initial zinc plate anode and the broken zinc plate anode at 520 discharge–charge cycle, (c) HRTEM images of the AgCu-MG after 1200 times charge-discharge cycle, (d) The charge-discharge curves of the AgCu-MG catalyzed cathode after 1200 times cycle. In this battery, the zinc anode and electrolyte were replaced.