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Electronic Supplementary Information (ESI)

Reliable Seawater Battery Anode: Controlled Sodium Nucleation via Deactivation of Current Collector Surface

Do Hyeong Kim,‡[a] Hongkyw Choi,‡[b] Dae Yeon Hwang,‡[a] Jaehyun Park,[a] Keun Soo Kim,[c] Seokhoon Ahn,[d] Youngsik Kim,[a] Sang Kyu Kwak,*[a] Young-Jun Yu,*[e] and Seok Ju Kang*[a]

[a]School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Korea. E-mail: skkwak@unist.ac.kr, sjkang@unist.ac.kr

[b]Materials & Components Basic Research Group, Electronics and Telecommunication Research Institute (ETRI), Daejeon 34129, Korea

[c]Department of Physics and Graphene Research Institute, Sejong University, Seoul 05006, Korea

[d]Institute of Advanced Composite Materials, Korea Institute of Science and Technology, Jeonbuk 55324, Korea

[e]Department of Physics, Chungnam National University, 99 Daehak-ro, Yuseong-gu, Daejeon 34134, Korea

*E-mail: skkwak@unist.ac.kr, yjyu@cnu.ac.kr, sjkang@unist.ac.kr

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1. Computational Details

Molecular dynamics (MD) simulations:

Modeling:

We constructed 4 surface model systems (pristine Cu (Cu), graphene coated Cu (Cu@G), partially surface-oxidized Cu (Cu_O), and graphene coated partially surface-oxidized Cu (Cu_O@G)) with 10.02 nm × 10.07 nm periodic 8-layerd Cu (111) surface using 14720 copper atoms and 3680 carbon atoms (for graphene-covered models), with partially surface-oxidized region by the most stable surface-oxidized Cu (111) surface (Cu(111)-1ML) configuration shown in Supporting Information Figure S23.[1] To investigate the Na^+ ion adsorption, a single layer of Na^+ ion (400 atoms) was placed on each surface. To avoid self-interactions, the height of the simulation box was extended to 50 nm to introduce the vacuum slab.

Simulation details:

All-atom molecular dynamics (MD) simulations were performed using the Forcite program [Materials Studio 2017 R2. Release 2017, San Diego, CA]. The COMPASS force was employed to describe the interaction between Na^+ ion and each surface model.[2] For oxygen atom and its surrounding copper atoms, we used Mulliken charge from the surface-oxidized Cu model obtained using DFT calculation (i.e., Cu: + 0.66, O: − 0.69). The cutoff distance was set to 15 Å for short-range van der Waals interactions. The Ewald summation method was used for the long-range electrostatic interactions.[3] For the isothermal state, the temperature of the system was controlled by Berendsen thermostat with a decay constant of 0.1 ps.[4] The time step for MD simulation was set to 1 fs. The initial model system was equilibrated for 100 ps at 298 K with NVT ensemble. After that, MD simulation was performed for 1 ns to investigate Na^+ ion adsorption at each surface. During the simulation, the lowest Cu layer was kept fixed. The two-dimensional density plot of Na^+ ion at each surface was analyzed with MD trajectories of the last 1 ns.

Density functional theory (DFT) calculations:

Modeling and energy calculation:

We constructed partially surface-oxidized Cu surface models with and without graphene coating to investigate the Na atom adsorption energy and the binding energy between two Na atoms on 4 difference surface sites (Cu, Cu@G, Cu_O, and Cu_O@G). A periodic 3-layered stable Cu (111) surface (25.18 Å × 8.72 Å) with 120 copper atoms and 80 carbon atoms (for graphene coated models) was used (Supporting Information Figure S24). For Na growth, we modeled a 12.29 Å × 13.08 Å periodic 3-layered stable Cu (111) surface with 90 copper atoms and 60 carbon atoms (for graphene coated models), as shown in Supporting Information Figure S25. We fixed the bottom layer of Cu for all DFT calculation models. For all graphene-coated models, the graphene lattice parameter was adjusted to fit the Cu (111) surface lattice parameter due to lattice mismatch (i.e. 2.04 %), and the most stable surface-oxidized Cu (111) surface (Cu(111)-1ML) configuration was used for all surface-oxidized models.[1] A vacuum space of over ~15 Å was introduced for all model systems.

Simulation details:

DFT calculations were performed using the DMol3 program to further understand the effect of surface on Na metal plating.[5, 6] Generalized gradient approximation (GGA) with Perdew-Burke-Ermzerhof (PBE) functional was used with the basis set of DNP 4.4.[7] Unrestricted spin-polarized calculations were performed. The Brillouin zone integration of Monkhorst Pack was utilized with Γ-point.[8] The convergence criteria for geometry optimization were 1.0

× 10^{-5} Ha for energy, 0.002 Ha/Å for force, and 0.005 Å for displacement. The self-consistent field convergence was less than 1.0 × 10^{-6} Ha, and the electron smearing value was set to 0.005 Ha. The core treatment was set to include the relativistic effect of all electrons on core electron. The long-range dispersion correction was taken into account with the semi-empirical DFT-D2 method suggested by Grimme.[9] The conductor-like screening model (COSMO) method was applied to all systems using the dielectric constant of DME (1,2-dimethoxy-ethane) at 25 °C (i.e., 7.3).[10]

Energy calculation:

The Na atom adsorption energy (E_{ads}) and the binding energy (E_{bind}) between two Na atoms were calculated as follows,

$$E_{ads} = E_{Total\_Na} - (E_{surface} + \mu_{Na}) \tag{S1}$$

$$E_{bind} = E_{Total\_biatom} - E_{surface} - 2\mu_{Na} \tag{S2}$$

where E_{Total_Na}, E_{Total_biatom}, and $E_{surface}$ are the total energy for Na atom adsorbed on the surface, energy of a Na-Na cluster adsorbed on the surface, and energy of the surface system, respectively. μ_{Na} represents the chemical potential of Na atom.

From the Na growth models, we calculated Na crystal formation energy (E_F) as follows,

$$E_F = (E_{total_{crystal}} - (E_{surface} - N_{Na}\mu_{Na}))/N_{Na} \tag{S3}$$

where $E_{total\_crystal}$ and $E_{surface}$ are the total energy for Na crystal with the substrate system and the energy of the surface system, respectively. N_{Na} represents the number of Na atoms in the system.

Contact angle and surface energy:

Surface free energy were calculated using Geometric mean and Harmonic mean equations. These equations are given as follows

Geometric mean equation

$$\gamma_l(1 + Cos\theta) = 2((\gamma_l^d\gamma_s^d)^{\frac{1}{2}} + (\gamma_l^p\gamma_s^p)^{\frac{1}{2}}) \tag{S4}$$

Harmonic mean equation

$$\gamma_l(1 + Cos\theta) = 4(\frac{\gamma_l^d\gamma_s^d}{\gamma_l^d + \gamma_s^d} + \frac{\gamma_l^p\gamma_s^p}{\gamma_l^p + \gamma_s^p}) \tag{S5}$$

where γ_l, γ_s, γ^d and γ^p are surface free energy of liquid, surface free energy of solid, dispersive surface free energy and polar surface free energy ($\gamma_{total} = \gamma^d + \gamma^p$). The use of Geometric mean equation and Harmonic mean equation would require contact angles as well as dispersive and polar components of surface free energy of two test liquids (Supporting Information Figure S14a). Solving equations would lead to γ_s^d, γ_s^p values for the surface. Using measured contact angles, surface free energy of Pristine Cu, Graphene on Cu, 6sec O_2 plasma treated graphene and Cu coated SiO_2 wafer were calculated (Supporting Information Figure S14b). Water and EG (ethylene glycol) were used as test liquids (Water: $\gamma_l^d = 21.8$, $\gamma_l^p = 51$ EG: $\gamma_l^d = 29$, $\gamma_l^p = 19$).

2. Supporting Figures

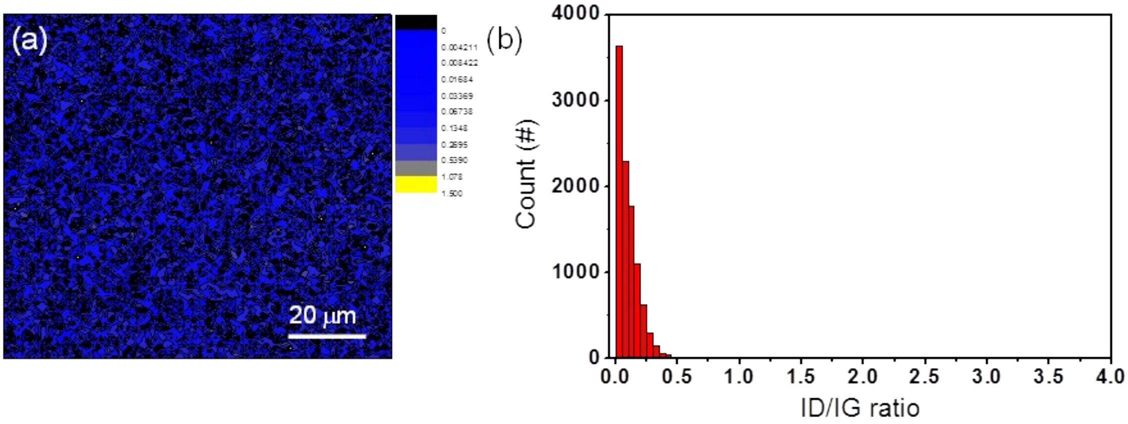


Fig. S1 (a) Raman mapping image of the I_D/I_G ratio of single layer graphene on Cu foil. (b) Histogram of the I_D/I_G intensity ratio (ratios < 0.5) in Raman mapping image from (a). Raman map is observed from 100 μm × 100 μm area.

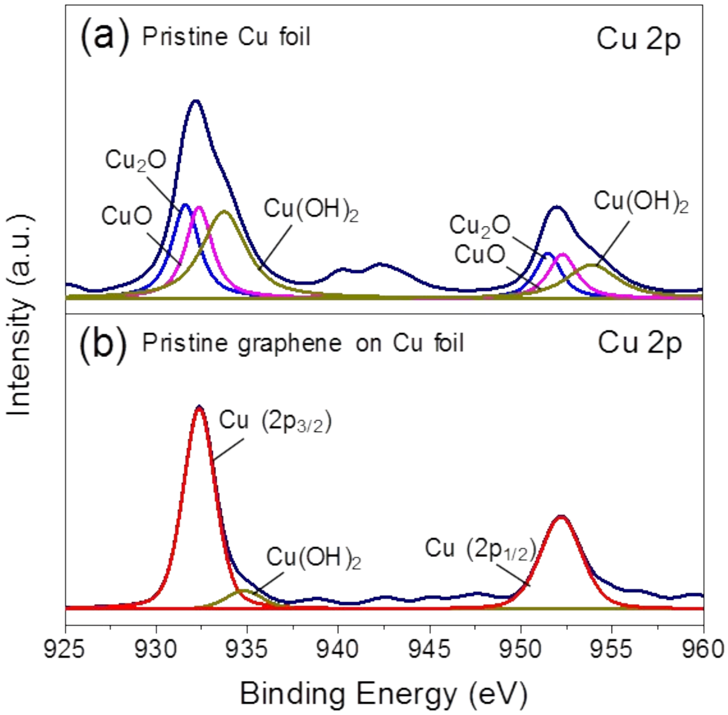


Fig. S2 XPS results from the (a) pristine Cu and (b) graphene coated Cu current collectors.

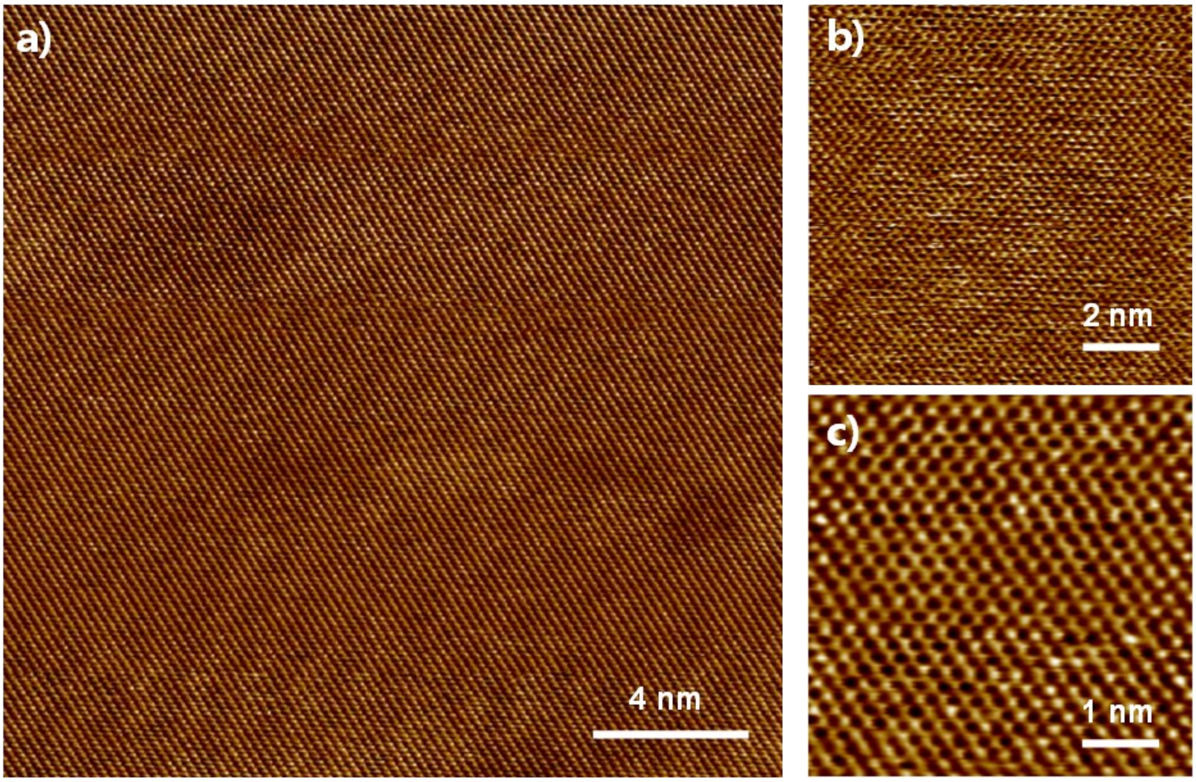


Fig. S3 STM images of single layer graphene on Cu current collector with different scan size. (a) 20 × 20 nm^2, (b) 10 × 10 nm^2, and (c) 5 × 5 nm^2.

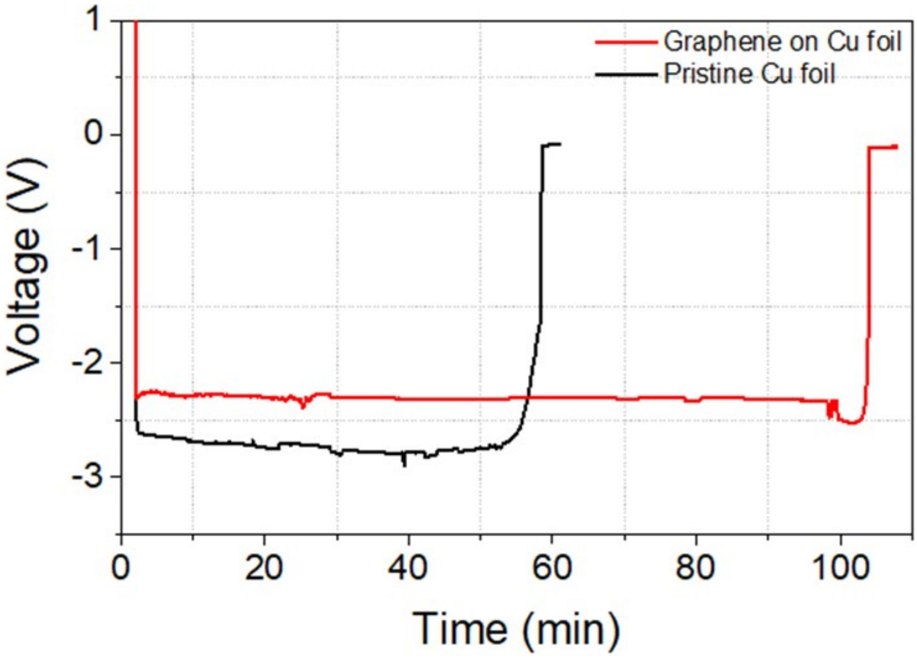


Fig. S4 Voltage responses of graphene on Cu and pristine Cu foils

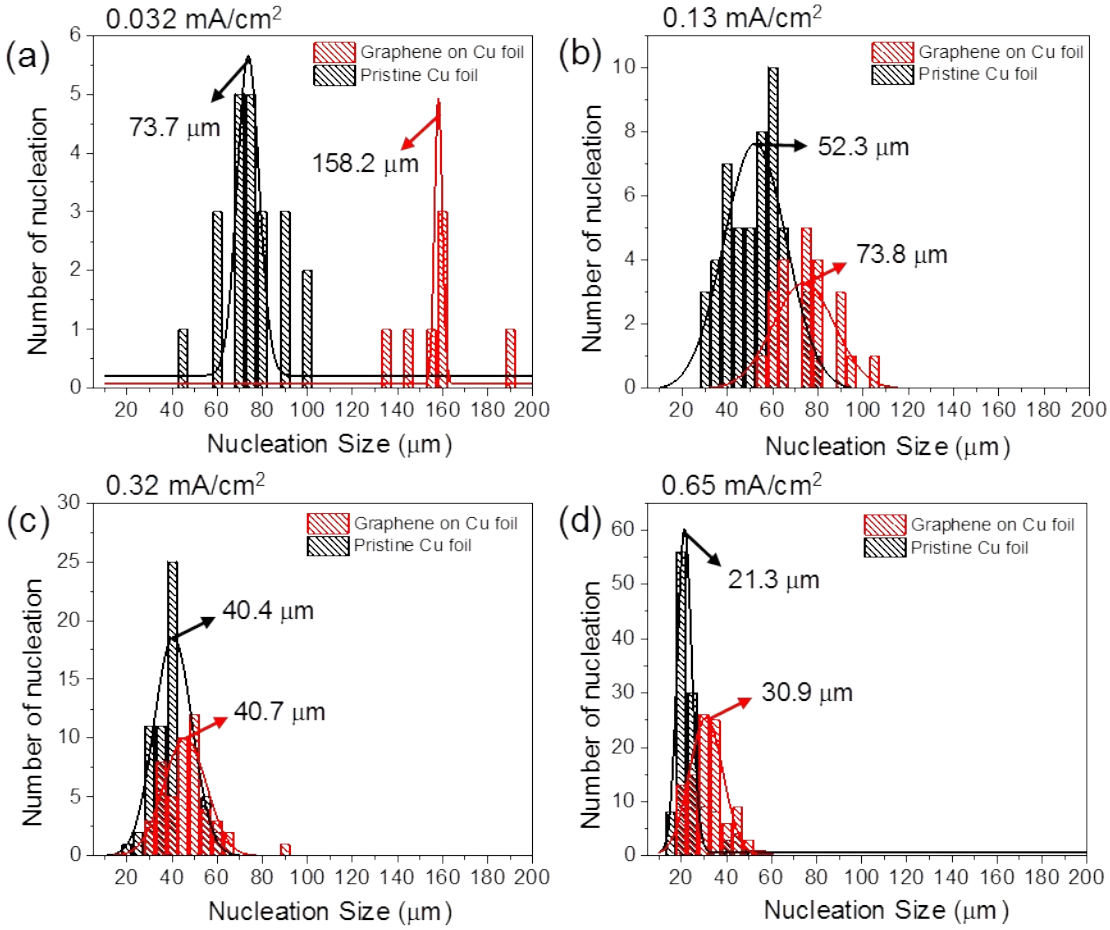


Fig. S5 Histograms of Na nucleation sizes versus number of nucleation on pristine Cu and graphene coated Cu current collector with a different current density of (a) 0.032 mA cm^{-2}, (b) 0.13 mA cm^{-2}, (c) 0.32 mA cm^{-2} and (d) 0.65 mA cm^{-2}, respectively. The total capacity is fixed of 0.1 mA h cm^{-2}.

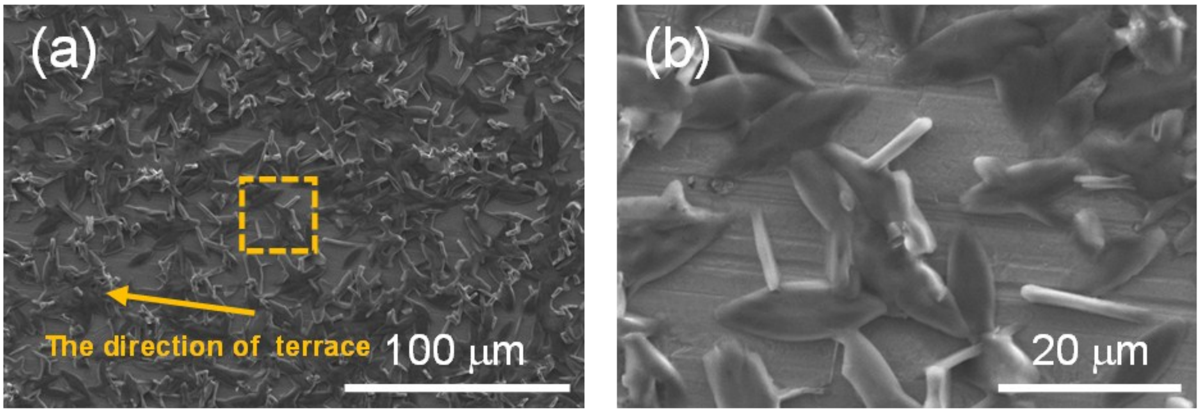


Fig. S6 (a) Top-view SEM images of Na metal growth on pristine Cu. (b) magnified image of yellow dot square in (a).

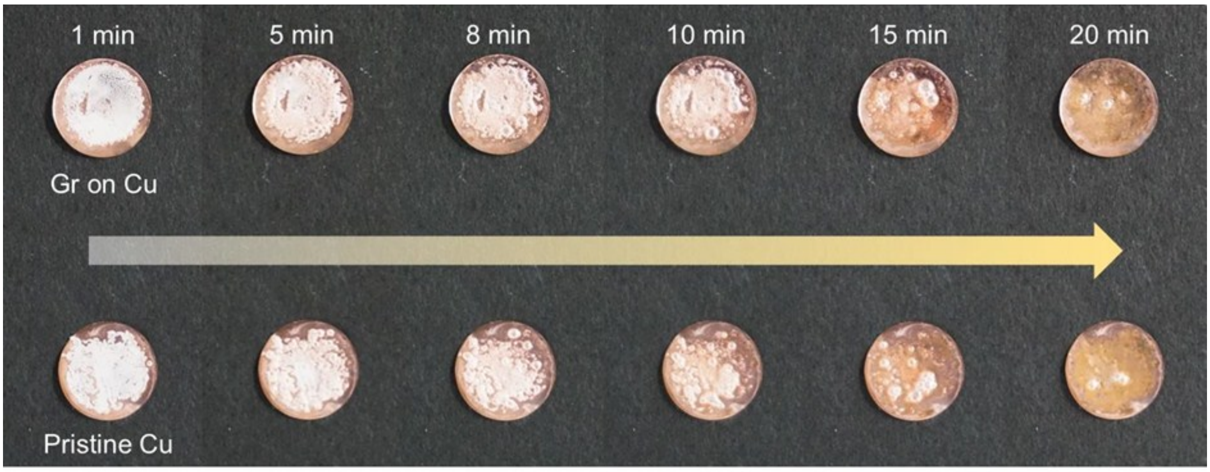


Fig. S7 Photographs of 0.53 mA h cm^{-2} Na on graphene on Cu and pristine Cu current collector after being exposed in the air.

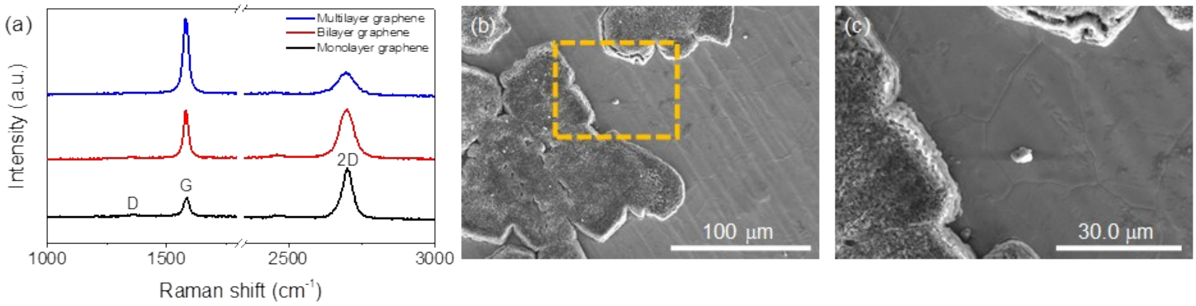


Fig. S8 (a) Raman spectra of transferred few layer graphene on 300 nm thick SiO_2. The intensity ratio between G and 2D indicates the number of graphene layer. Plane view SEM image of (b) Na island on multi-layered graphene and (c) magnified image of yellow dot square in (b).

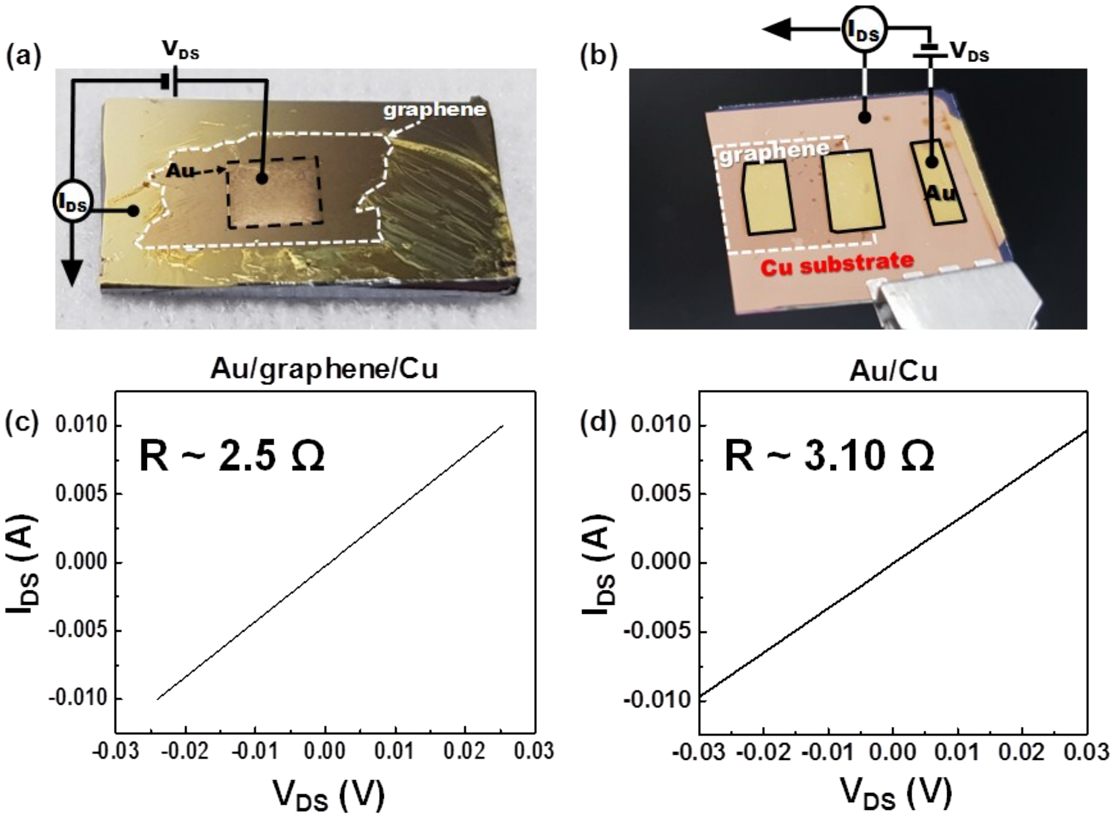


Fig. S9 (a) Photograph image of multi-layered graphene contacted with Au metal on bottom and top surface. (b) Photograph image Cu substrate with Au metal contacted on Cu surface. (c) I-V curves of Au/graphene/Au and (d) Au/Cu contact conditions.

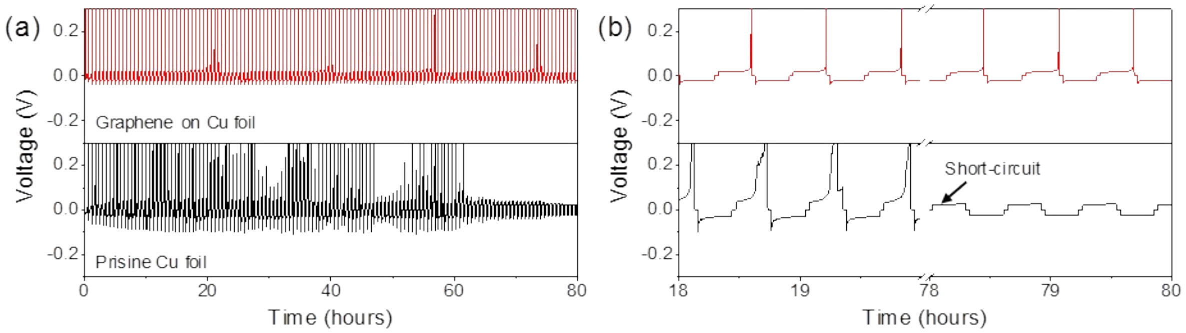


Fig. S10 (a) Chronopotentiometry plots and (b) magnified voltage profiles of graphene covered Cu (red line) and pristine Cu (black line) current collectors. The cycling was performed with ±0.65 mA cm^{-2} for 1000 sec.

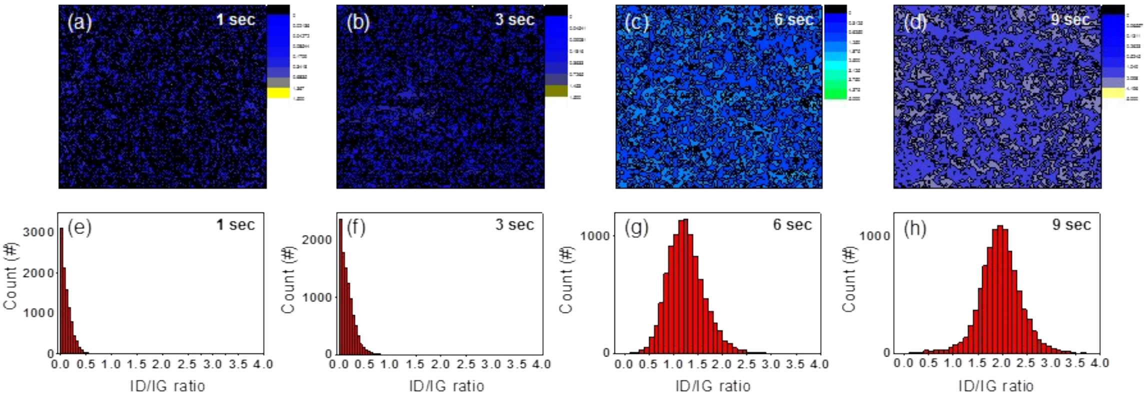


Fig. S11 Raman maps of the I_D/I_G ratio of (a) 1 sec, (b) 3 sec, (c) 6 sec and (d) 9 sec O_2 plasma treated sample. (e–h) Histograms of the I_D/I_G intensity ratio in Raman mapping images from (a–d). Raman maps are observed from 100 μm × 100 μm areas.

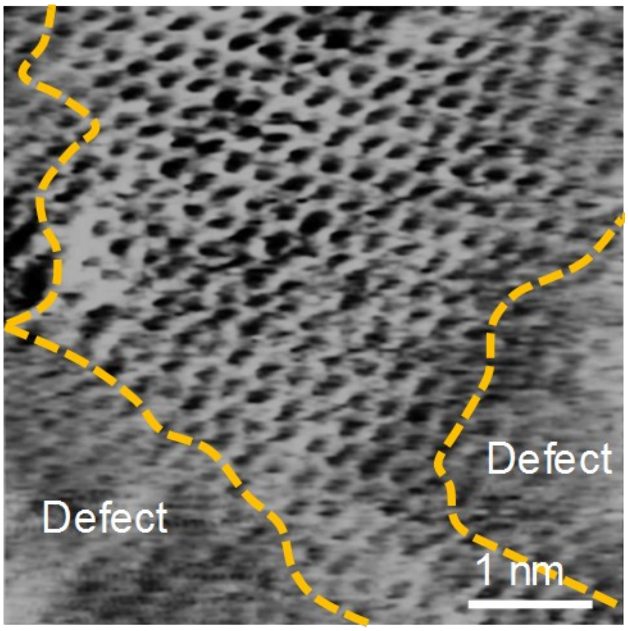
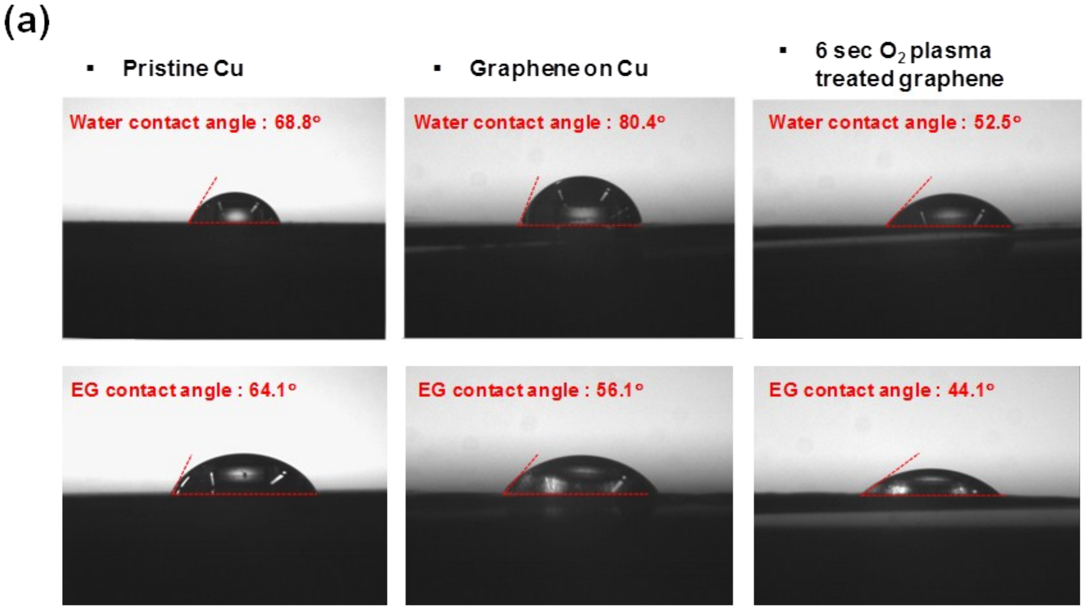


Fig. S12 Atomically resolved STM image of deteriorated graphene after 6 sec O_2 plasma exposure time. The yellow dot lines indicate the damage area on the Cu foil.



(b)

Surface	Geometric mean			Harmonic mean		
	γ_s^d (mJ/m^2)	γ_s^p (mJ/m^2)	γ_s (mJ/m^2)	γ_s^d (mJ/m^2)	γ_s^p (mJ/m^2)	γ_s (mJ/m^2)
Pristine Cu	2.79	34.21	37.00	6.43	32.41	38.84
Graphene on Cu	20.44	8.95	29.39	15.14	16.21	31.35
6 sec O$_2$ plasma treated graphene	4.69	46.02	50.71	10.76	38.92	49.68

Fig. S13 (a) Contact angle measurements for pristine Cu, graphene on Cu and 6 sec O$_2$ plasma treated graphene using water and EG as test liquids. (b) Dispersive and polar components of surface free energy of Contact angle measurements for pristine Cu, graphene on Cu, and 6 sec O$_2$ plasma treated graphene surfaces obtained from Geometric and Harmonic mean equations.

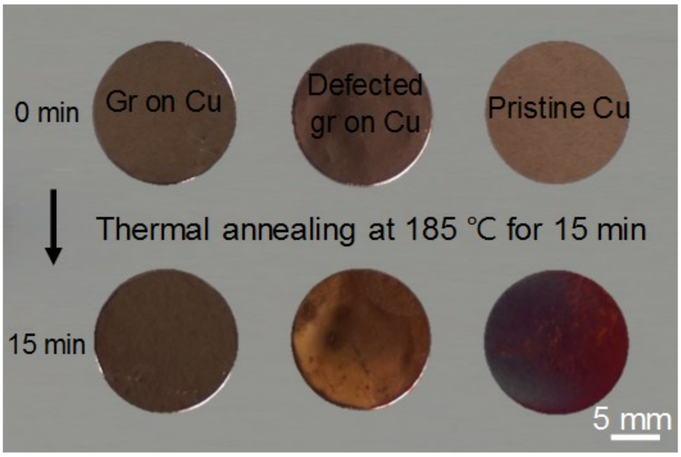


Fig. S14 A photograph of color change of Graphene coated Cu, Defected graphene coated Cu and pristine Cu. The three samples were thermally annealed in air for 15 min at 185 °C.

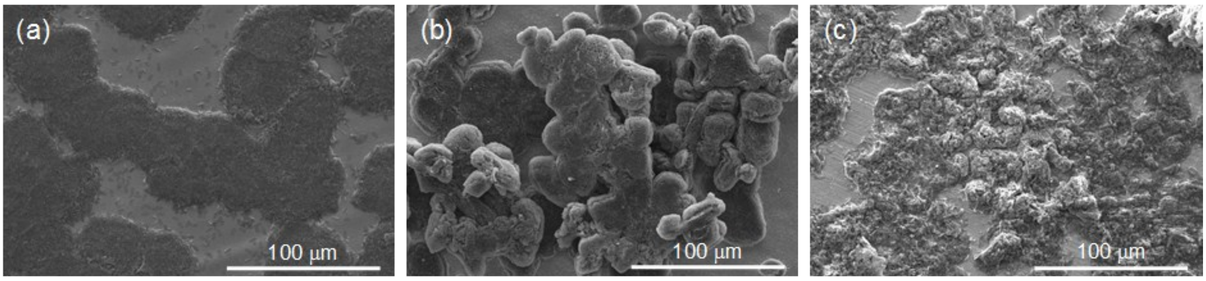


Fig. S15 The SEM image of plated Na metal on (a) thermally annealed graphene coated Cu foil (b) thermally annealed defected graphene coated Cu foil and (c) thermally annealed Cu at 0.65 mA cm^{-2} for total capacity of 0.1 mA h cm^{-2}.

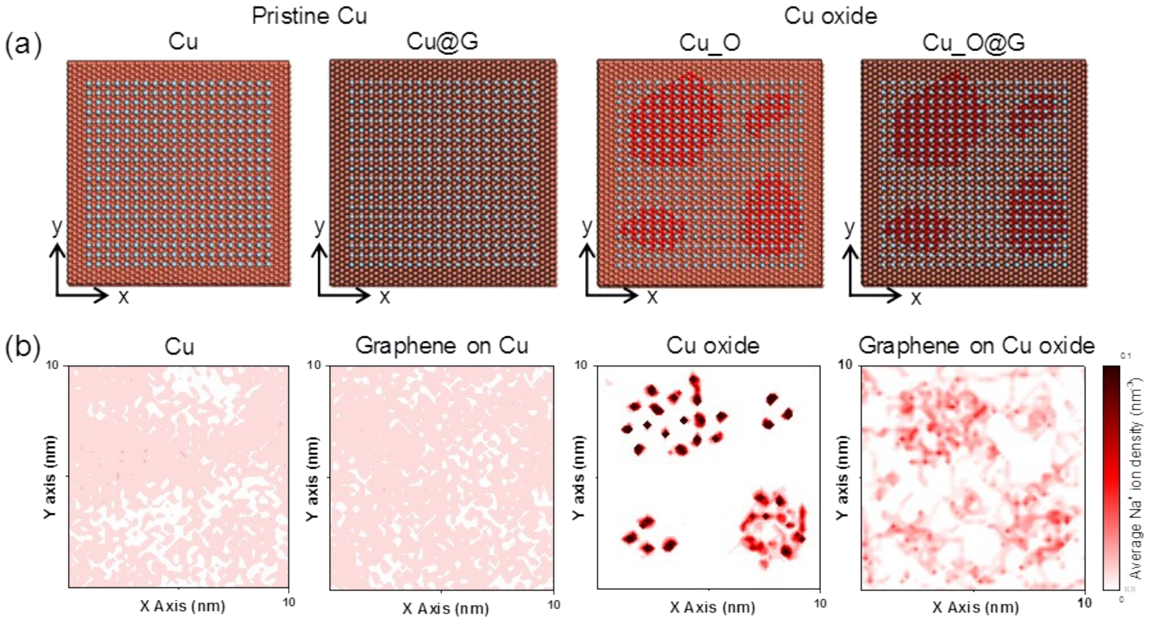


Fig. S16 (a) Initial configuration of 4 type model systems (Cu, Cu@G, Cu_O and Cu_O@G) to investigate Na^+ ion adsorption tendency and site on each surface. (b) The two-dimensional density plot of Na^+ ion within 5 Å in the vertical direction from the surface during 1 ns. Note that orange, red, sky blue spheres indicate Cu, O and Na atoms, respectively. Dark-gray honeycomb network indicates the graphene layer.

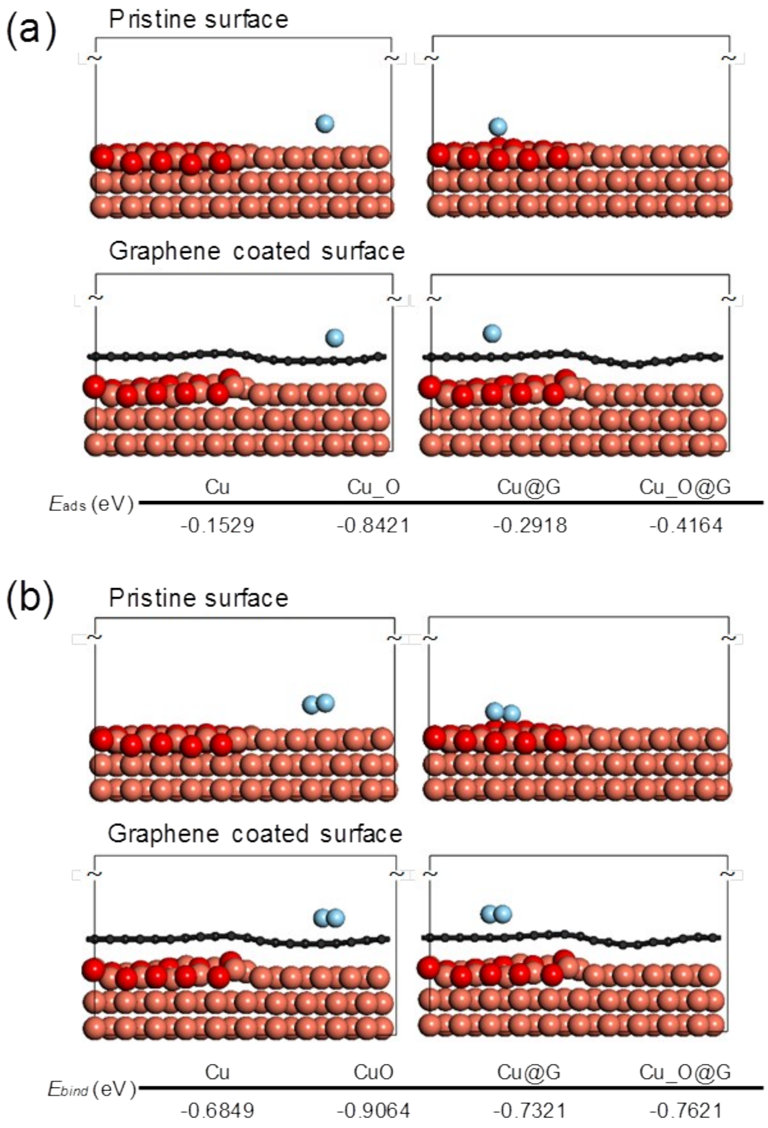


Fig. S17 (a) Optimized structures of Na atom adsorption on each Cu, Cu_O, Cu@G and Cu_O@G site and adsorption energy of Na on each site. (b) Optimized structure of two Na atom cluster configuration on each Cu, Cu_O, Cu@G and Cu_O@G site and binding energy between two Na atoms on each site. Note that orange, red, sky blue spheres indicate Cu, O and Na atoms, respectively. Dark-gray honeycomb network indicates the graphene layer.

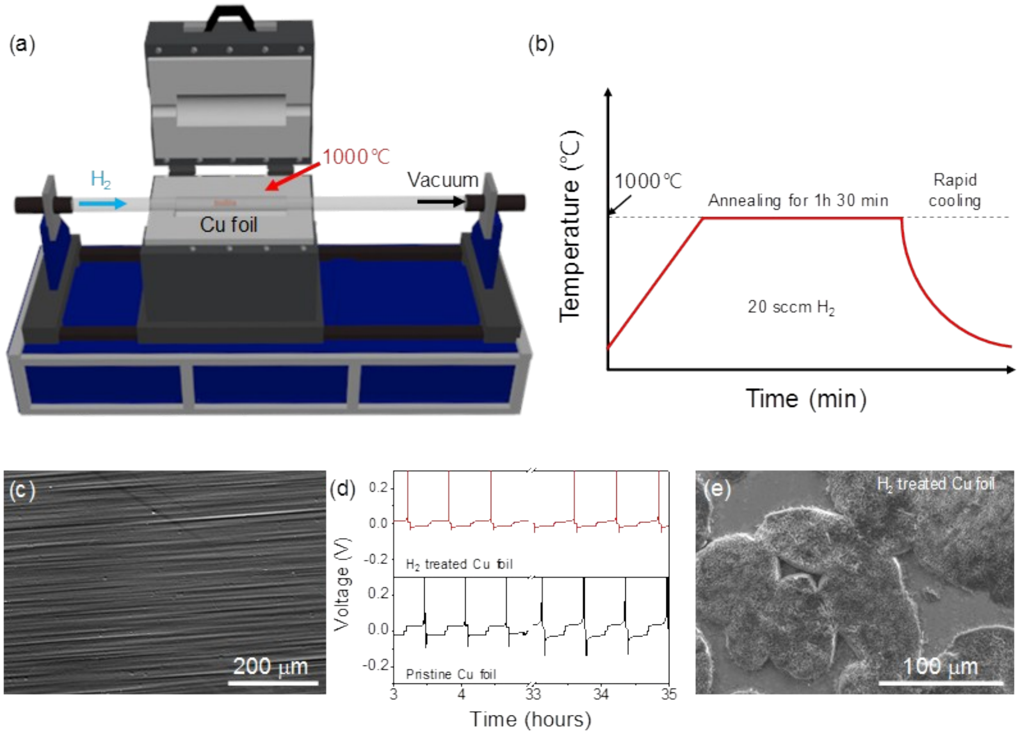


Fig. S18 (a) Schematic diagram of tube furnace set-up and (b) heating profile. (c) Top-view SEM image of H_2 treated Cu foil. (d) Galvanostatic plating-stripping profiles of H_2 treated and pristine Cu foils (±0.32 mA cm^{-2} for 1000 sec). (e) SEM image of island like plated Na metal on H_2 treated Cu foil (0.1 mA h cm^{-2}).

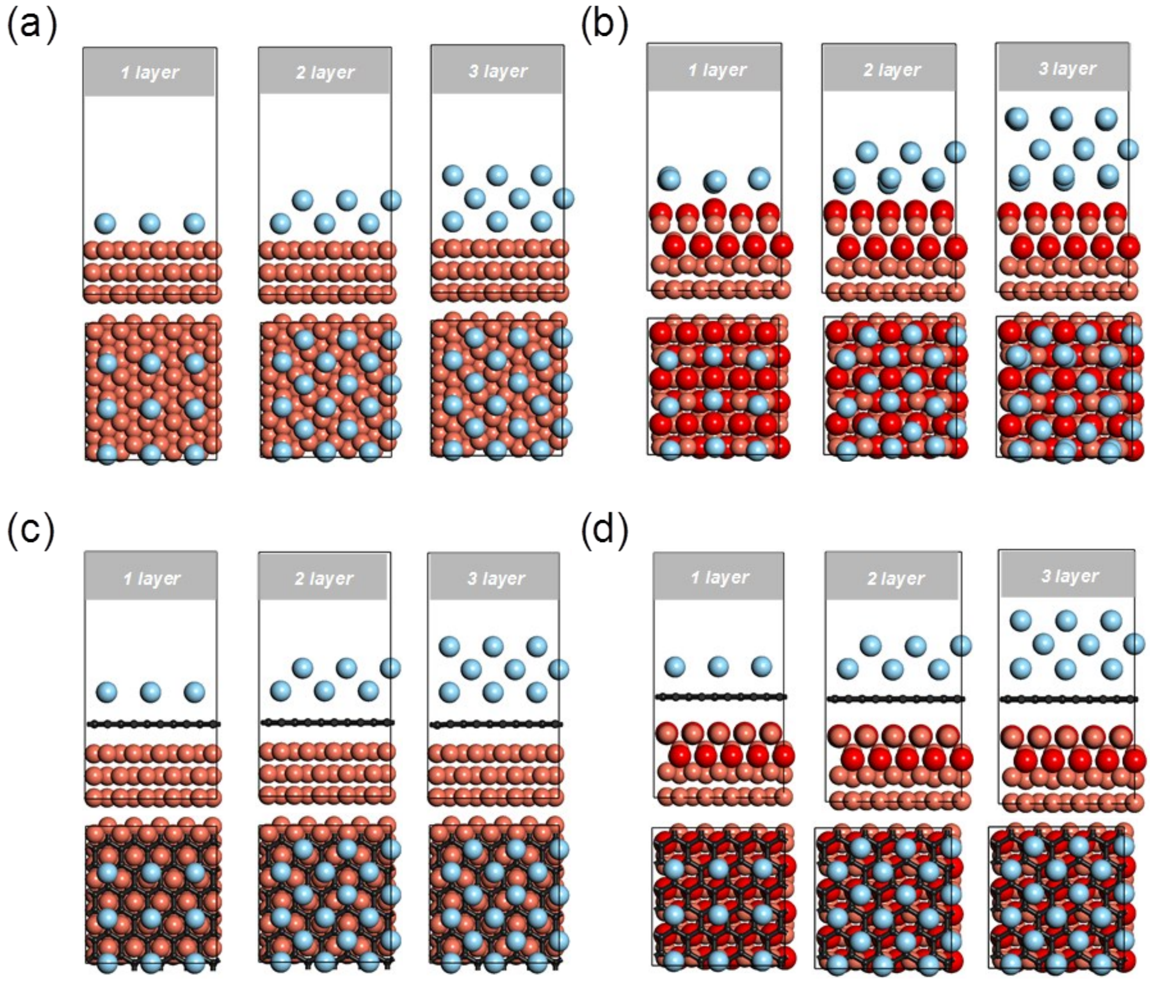


Fig. S19 Optimized structures of Na crystal on (a) pristine Cu, (b) surface-oxidized Cu (Cu_O), (c) graphene coated Cu (Cu@G), and (d) graphene coated surface-oxidized Cu (Cu_O@G) substrates up to 3 Na crystal layers. Note that orange, red, sky blue spheres indicate Cu, O and Na atoms, respectively. Dark-gray honeycomb network indicates the graphene layer.

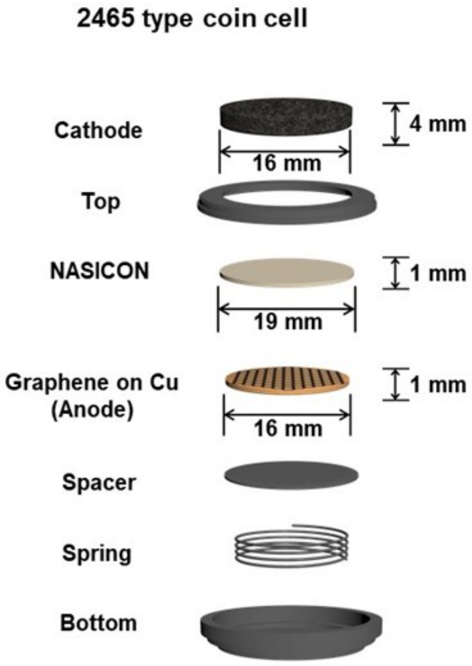


Fig. S20 Schematic of components of modified 2465 type coin cell for seawater battery.

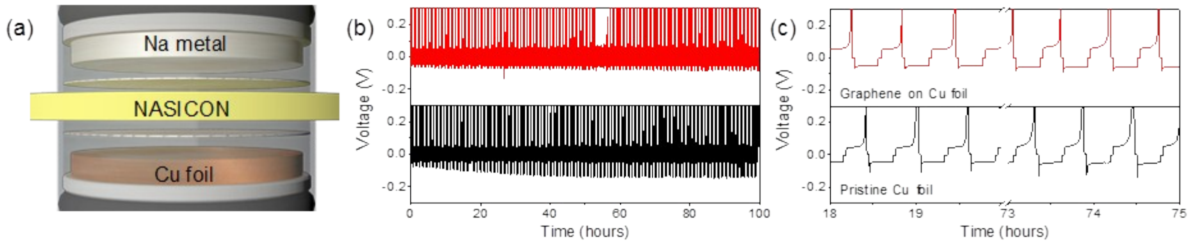


Fig. S21 (a) Schematic of home built symmetric cell with NASICON separator. (b) Chronopotentiometry plots and (c) magnified voltage profiles of Na/NASICON/graphene and Na/NASICON/Cu symmetric cells.

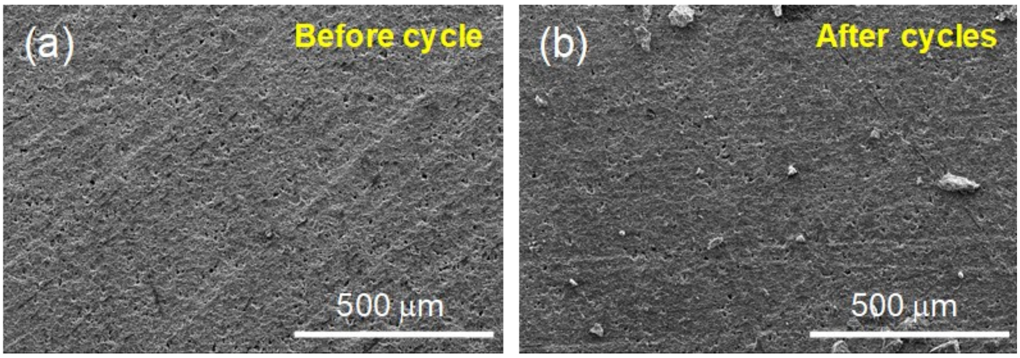


Fig. S22 Plane view SEM images of NASICON (a) before and (b) after cycles.

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