Electronic Supplementary Information:

Brain-coral inspired metal/carbon hybrid using an agarose gel for ultra-fast charge and discharge supercapacitor electrodes

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Supplementary Methods

1. Fabrication of bicontinuous carbon and 3D Au composite.

A 2 % (w/v) solution of agarose gel with dimensions of 1 cm × 2 cm × 0.5 cm was immersed in a 100 mM $HAuCl_4$ solution for 18 h at room temperature in sealed container. The gold precursors ($HAuCl_4$) inside the pores of the agarose gel were then completely reduced by treatment with an excess of sodium borohydride ($NaBH_4$), and washed with de-ionized water. The resulting gold/agarose gel composite was dried in a vacuum desiccator at room temperature before carbonization at 800 ℃ for 4h under Ar or NH_3 atmosphere.

2. Physicochemical characterization.

The surface morphology and composition of the Au/C composites were characterized using a scanning electron microscopy (SEM, Carl Zeiss, SUPRA 55VP). X-ray photoelectron spectroscopy (XPS, Karatos, AXIS-HSi), and X-ray diffractrometer (XRD, Rigaku, D/max-2200) were utilized to investigate the crystalline and elemental structure of composite. Bright-field TEM image was collected by high-resolution TEM (HR-TEM, JEOL, JEM-3010).

3. Electrochemical characterization.

Electrochemical tests were performed using a standard three-electrode system (Iviumstat electrochemical analyzer, Ivium Technology) with a saturated Ag/AgCl as a reference electrode and platinum counter electrode. The working electrodes were prepared by coating the carbon materials (3DMC, activated carbon, graphite) and polytetrafluoroethylene (PTFE) as a binder on stainless steel (SUS) mesh. The analyses were conducted in 2M Li_2SO_4 aqueous electrolyte.

4. Calculations.

The specific capacitance (F g^{-1}) was calculated from the cyclic voltammograms (CVs) according to the following equation:

$$C = \frac{In_{CV}}{v \times \Delta V \times m} \qquad (1)$$

where, In_{cv} is the area of integral for the discharged CV curve (AV), v is the sweep rate (V s^{-1}), ΔV is the potential window (V) and m is the mass of electrode materials (g).[S1]

The specific power (P, W kg^{-1}) at certain scan rate v (V s^{-1}) was calculated by integrating discharged area (IV) of CV curve as follows:[S2]

$$P = \int_{V_1}^{V_2} I/m \, dv \qquad (2)$$

where the V_1 is 0.0 V and the V_2 is 0.8 V.

And the specific energy W (Wh kg^{-1}) was obtained using the following equation:[S2]

$$W = \frac{V_2 - V_1}{v \times 3600} \times \int_{V_1}^{V_2} \frac{I}{m} \, dv \qquad (3)$$

The discharge/charge energy ratio (μ) was calculated as following equation:

$$\mu = \frac{W_d}{W_c} \times 100 \, \% \qquad (4)$$

where W_d and W_c are the discharge and charge specific energy, respectively. The discharge and charge specific energy (W, Wh kg^{-1}) values at certain scan rate v (V s^{-1}) were calculated by integrating discharged and charged area of CV curve by equation (3).

Supplementary Figures
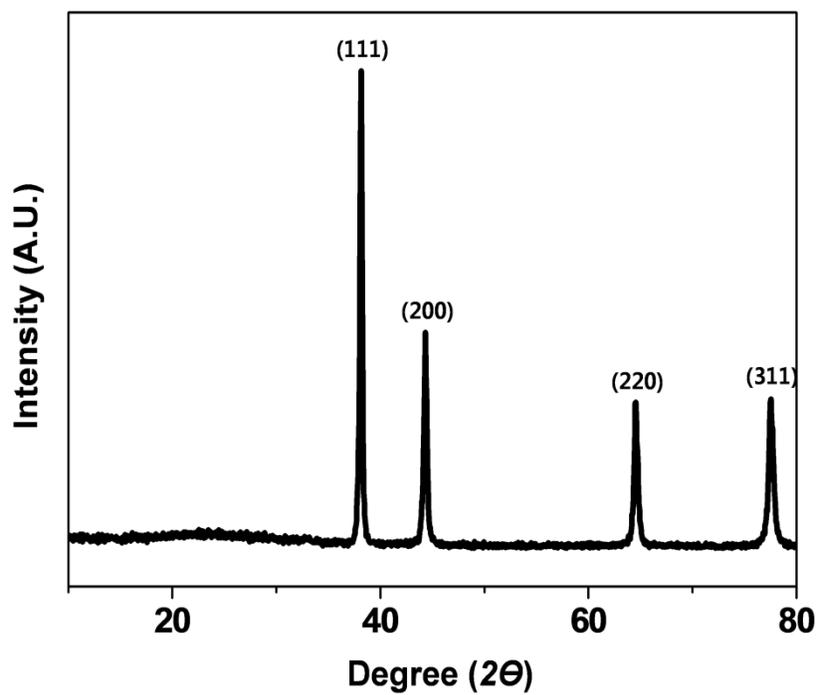
Fig. S1. Crystalline structure of 3DMC. All Bragg reflectrions, observed in the XRD spectra, are indexed on the basis of the fcc structure of Au. Therefore, 3DMC consists of amorphous carbon and Au with no peaks corresponding to graphitic carbon.
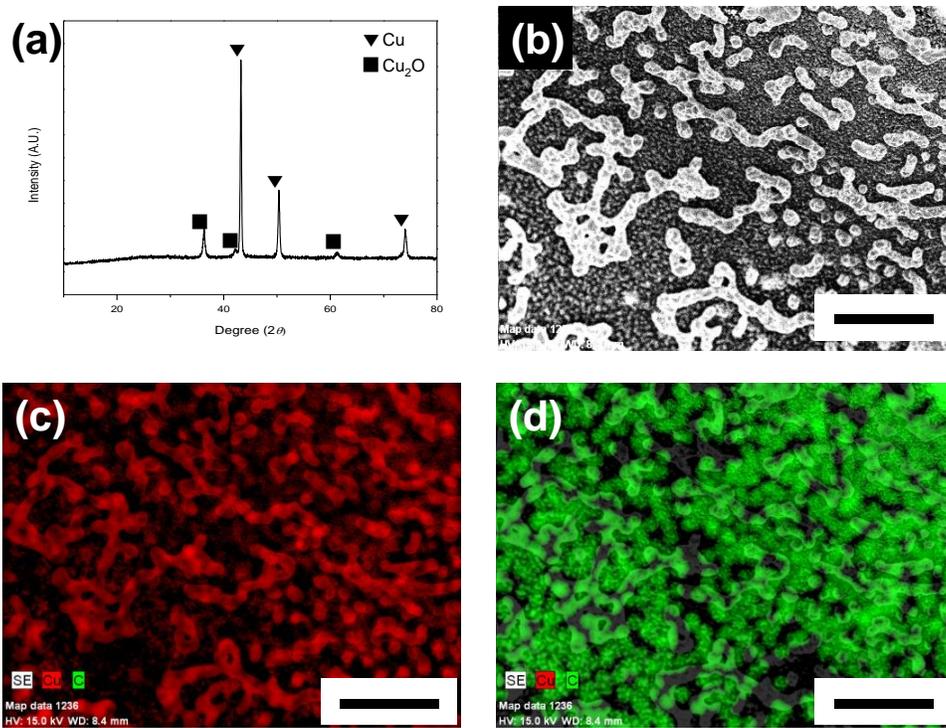
Fig. S2. Cu-based 3DMC. (a) Crystalline structure of Cu-based 3DMC, the observed in XRD spectra, indicates the co-existence of amorphous carbon and partially oxidized Cu. (b) SEM image of Cu/C bicontinuous structure. EDS atomic analysis results of Cu-based 3DMC; (c) copper and (d) carbon. All scale bars are 30 μm.
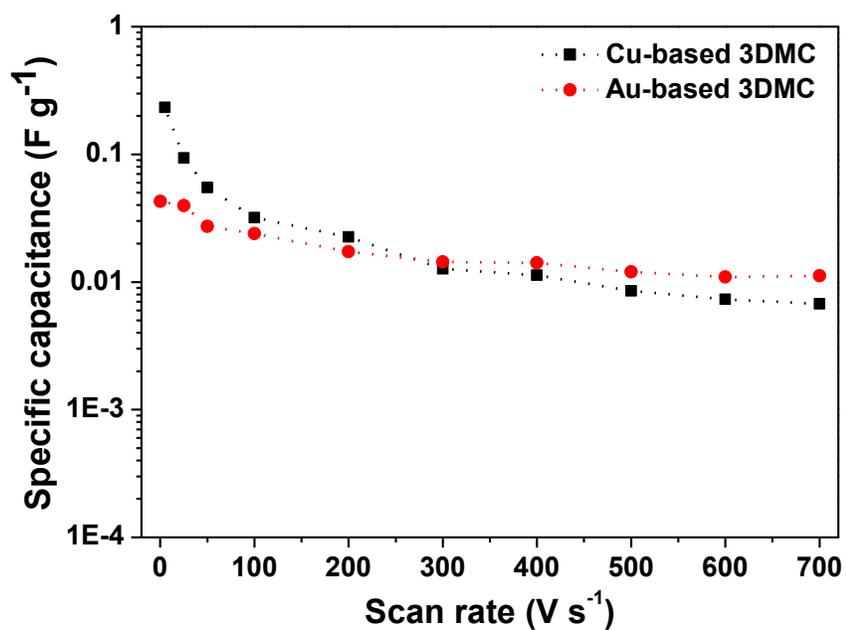
Fig. S3. Specific capacitance *versus* scan rate for Cu-based 3DMC (black) and Au-based 3DMC (red) electrode. Due to the partially oxidized 3D Cu, rate capability of carbon/Cu hybrid remained slightly below that of carbon/Au hybrid.
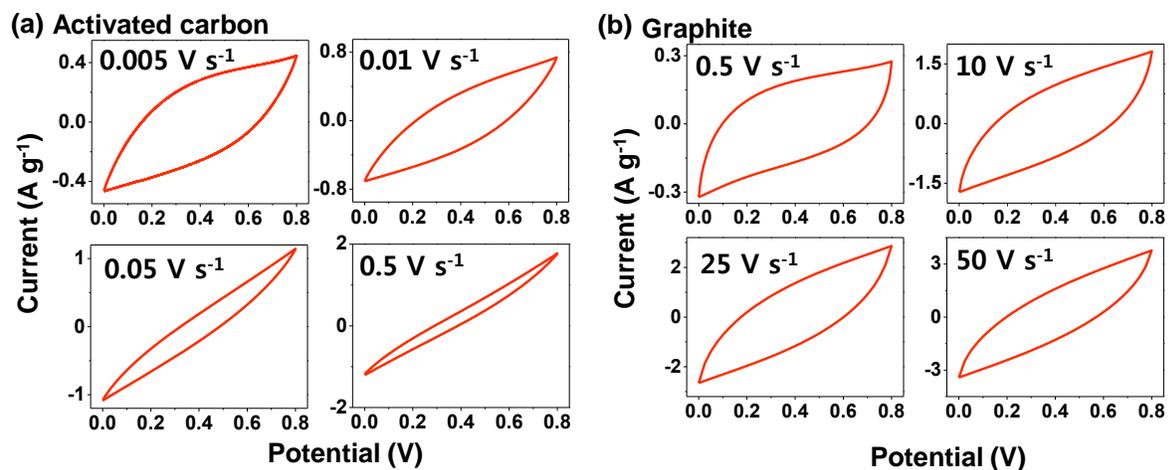
Fig. S4. Cyclic voltammograms for commercial activated carbon (a) and graphite (b) electrodes obtained at different scan rates.
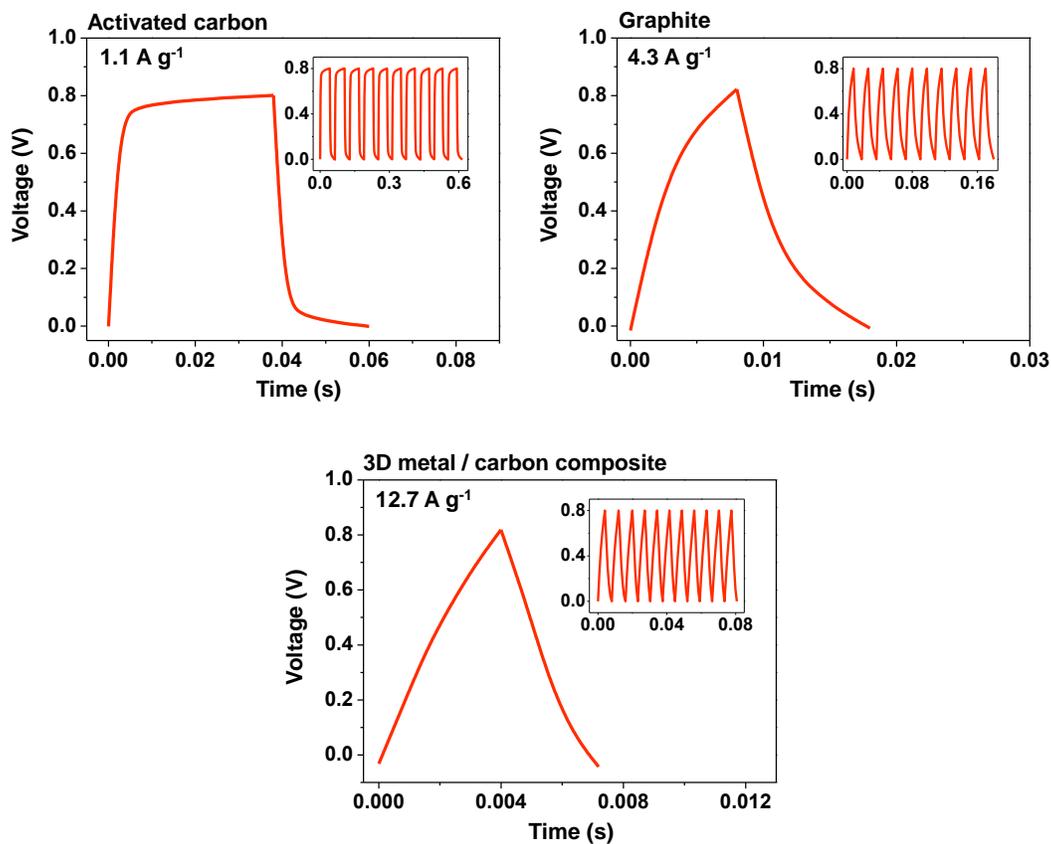
Fig. S5. Charge-discharge curves (voltage vs. time) for activated carbon, graphite and 3DMC electrodes. The specific current of activated carbon, graphite and 3DMC electrode are 1.1 A g^{-1}, 4.3 A g^{-1}, and 12.7 A g^{-1}, respectively. Each values of specific current were determined by the peak currents in the CV analysis at a scan rate of 0.5 V s^{-1}, 100 V s^{-1} and 500 V s^{-1}, respectively.
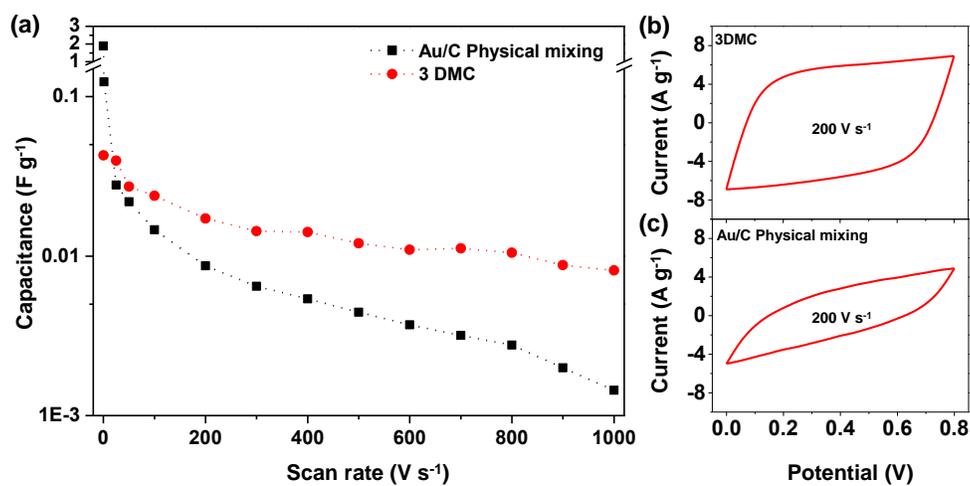
Fig. S6. (a) Specific capacitance of 3DMC and Au particle/carbonized agarose composite electrode as a function of scan rate. Cyclic voltammograms for 3DMC (b) and Au particle/carbonized agarose composite (c) obtained at scan rate of 200 V s^{-1}. Amorphous carbon obtained by carbonizing an agarose gel and Au particles prepared by aqueous reduction of HAuCl$_4$ were mixed by ball-milling.
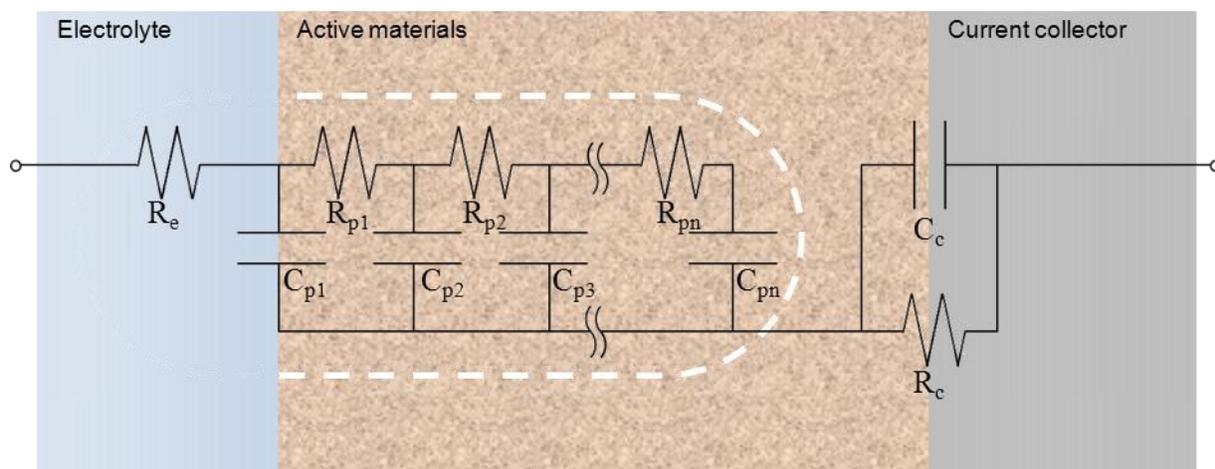
Fig. S7. Equivalent circuit model used to interpret the measured impedance spectra of the electrodes. These elements include electrolyte resistance (R_e), capacitance (C_c) and resistance (R_p) from ion migration through the inner pore structure (*De Levie* model). In the case of activated carbon and graphite electrodes, this circuit acceptably simulates the results of the Nyquist plot (Fig. 3(a)). On the other hand, the equivalent circuit of 3DMC is reduced to a simple RC circuit, because the pore structure resistance and charge transfer barriers between the electrode and current collector are negligible.
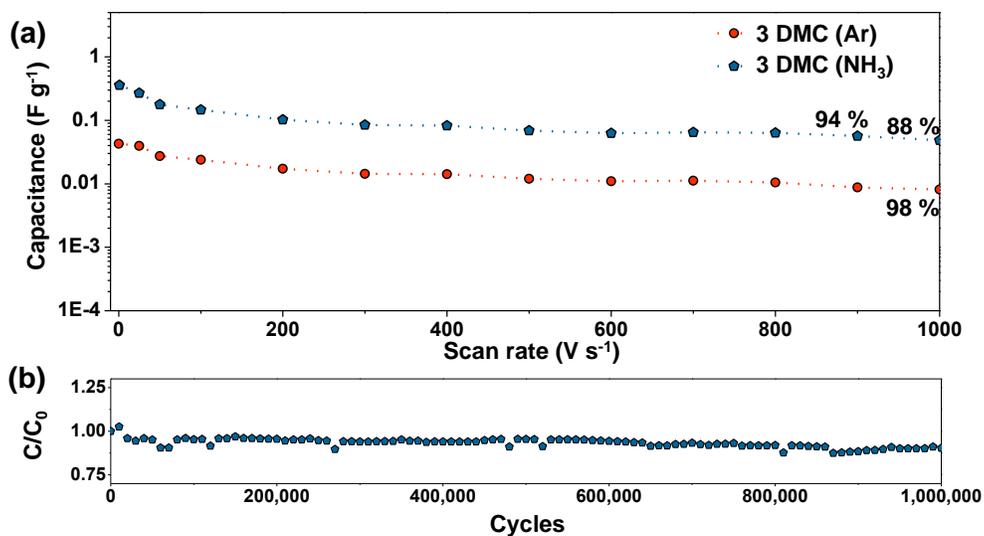
Fig. S8. (a) Comparison of the specific capacitance of Ar, NH$_3$ carbonized 3DMC electrode as a function of scan rate. NH$_3$ carbonized electrode (blue) show 7 times higher specific capacitance than that of Ar carbonized electrode (red). (b) Stability test during the 1,000,000 charge/discharge.
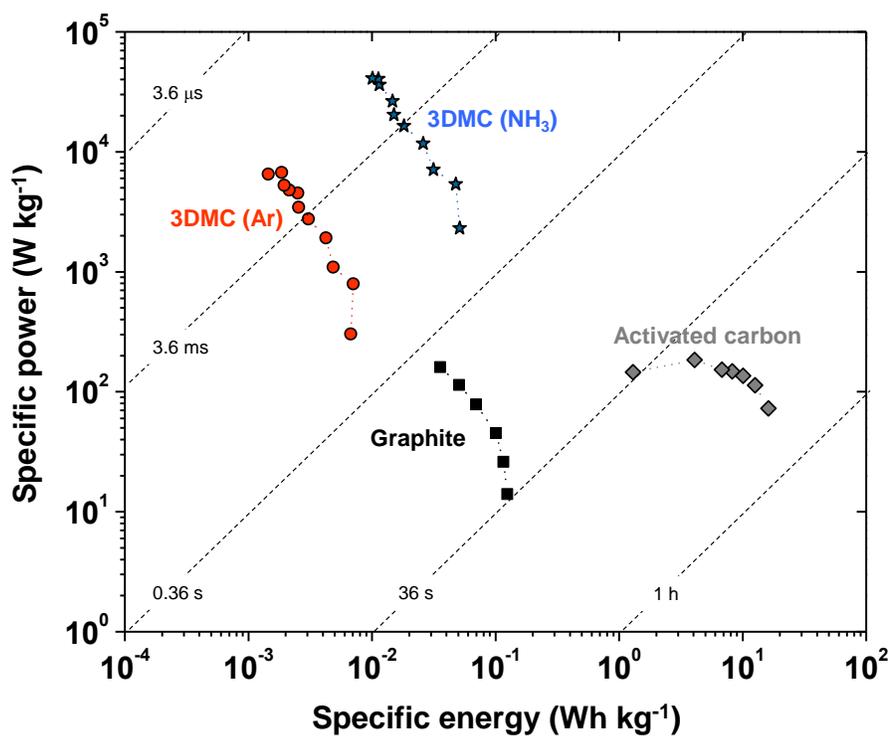
Fig. S9. Ragone plot (specific power against specific energy) for prepared 3DMC (Ar, NH$_3$), graphite, activated carbon-based electrodes. Times shown in plot indicate the time constants of each material, which are calculated by dividing the specific energy by the power.

References

S1. I. Nam, G. −P. Kim, S. Park, J. Park. N. D. Kim and J. Yi, *Nanoscale*, 2012, **4**, 7350.

S2. D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, P.-L. Taberna and P. Simon, *Nat. Nanotechnol.*, 2010, **5**, 651.