Supporting Information

Highly Energetic Flexible All-Solid-State Asymmetric Supercapacitor With Fe_2O_3 and CuO Thin Films

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1. Preparation of Fe_2O_3 and CuO thin film:

In present work, two different approaches for deposition of Fe_2O_3 and CuO thin films electrodes were used. Fe_2O_3 thin films were developed by simple successive ionic layer adsorption and reaction (SILAR) method using four beakers system [1]. The schematic of SILAR method is shown in Fig. S1. The solution of 0.01 M $FeCl_3$ as a cationic precursor and 1 M NaOH as an anionic precursor were used. Initially, well cleaned flexible stainless steel (SS) substrate was immersed in cationic precursor for 10 s for adsorption of Fe^{+3} species. Then substrate was rinsed in DDW for 5 s to remove loosely bound species. After that substrate was immersed in anionic precursor for 10 s where OH^- ions react with Fe^{+3} to produce Fe_2O_3. Again substrate was rinsed in DDW for removal of loosely bound species. Such a 120 cycles were repeated for well uniform deposition of Fe_2O_3 thin film along entire substrate.

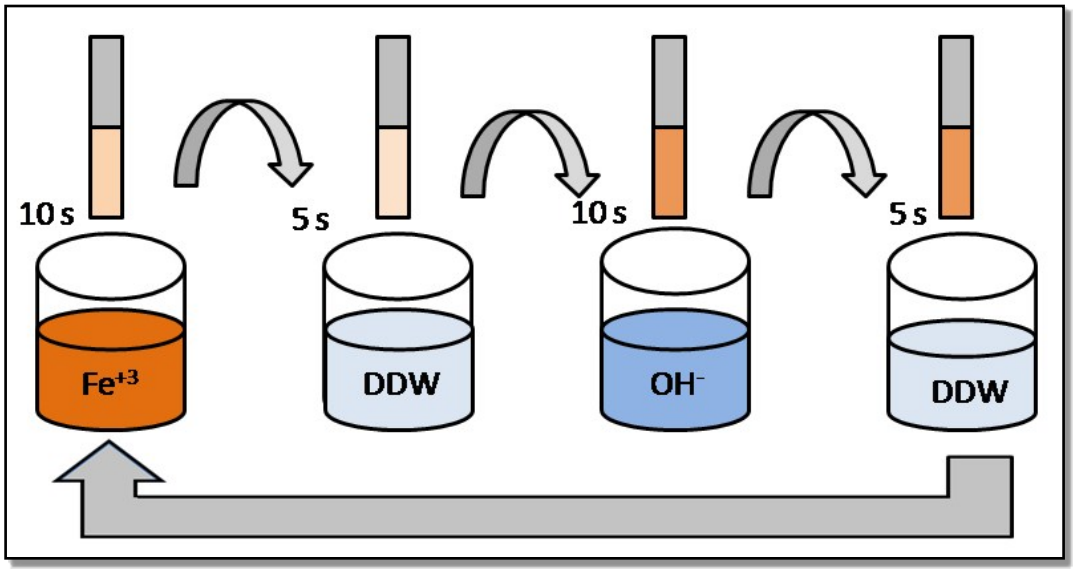

Fig. S1 Schematic of SILAR method used for preparation of Fe_2O_3 thin films

CuO thin films were deposited by simple and inexpensive chemical bath deposition (CBD) method [2]. The schematic of CBD method is shown in Fig. S2. A solution of 0.01 M $CuSO_4$ as a source of copper while liquid ammonia as a complexing agent were used for preparation of CuO thin film. Ammonia is added to a 0.01 M $CuSO_4$ solution until pH becomes ~10 where a transparent blue solution is formed. A well cleaned flexible SS substrate was used for deposition and the deposition was carried out at 353 k for 4 hrs.

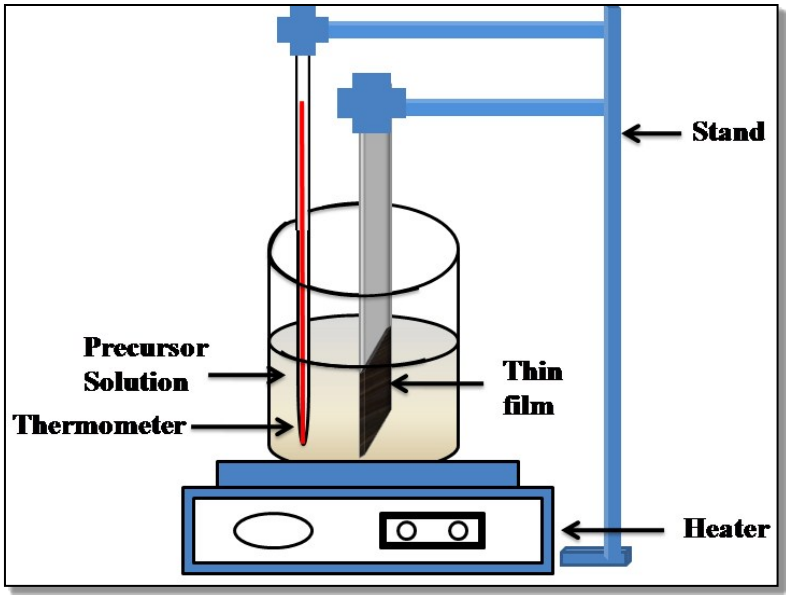

Fig. S2 Schematic of CBD method used for preparation of CuO thin films

2. Preparation of CMC-Na_2SO_4gel electrolyte

For fabrication of symmetric as well as asymmetric devices, carboxymethyl cellulose-sodium sulphate (CMC-Na_2SO_4) was used as a gel and also as a separator. It was prepared by dissolving 2 gm of CMC and 2 gm of Na_2SO_4 in 30 ml of DDW under constant stirring at 343 K. Then solution was constantly stirred at room temperature until it becomes sufficiently viscous. This solution was used as a gel electrolyte for SCs fabrication [3].

3. Fabrication of solid state SCs

The elementary structure of device consists of two material electrodes and a separator that prevents physical contact of the electrodes but allows ion transfer between them. Firstly, edges of two electrodes were made non-conducting by insulating band, separately, to avoid electrical contact. The CMC-Na_2SO_4 gel electrolyte was sandwiched between both electrodes and electrical contacts was made at electrodes. As prepared set up was packed by insulating band. The device was set under pressure of 1 ton for 5 min. to get good contact between electrode and gel electrolyte and to avoid loose binding or air gap. In fabrication of symmetric

device, similar thin films (Fe_2O_3 and CuO) were used as anode as well as cathode while in fabrication of asymmetric device Fe_2O_3 thin film was used as an anode while CuO thin film as a cathode. As two different electrodes materials are used in fabrication of asymmetric device, the balancing of mass ratio from cathode to anode is done by following equation [4],

$$\frac{m_+}{m_-} = \frac{C_-}{C_+} \times \frac{\Delta E_-}{\Delta E_+} \qquad (1)$$

where, m_+, m_-, C_+, C_-, ΔE_+, ΔE_- are the mass, specific capacitance, working potential window of cathode and anode, respectively.

4. Electrochemical parameters

The electrochemical features of fabricated symmetric and asymmetric flexible solid state SC devices were studied by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) techniques. CV is used to calculate the specific capacitance of devices using following equation,

$$C_s = \frac{1}{m \times v(V_c - V_a)} \int_{V_a}^{V_c} I(V)dV \qquad (2)$$

Where, C_s is the specific capacitance (F g^{-1}), V is the potential scan rate (mV s^{-1}), (V_c–V_a) is an operational potential window (V), I(V) is the current response (mA) and m is deposited mass of electrode material (g) for a device with unit area.

GCD studies are also used to calculate the specific capacitance by using following equation,

$$C_s = \frac{I_d \times T_d}{\Delta V \times m} \qquad (3)$$

where, Cs is specific capacitance (F g^{-1}), I_d is discharge current (mA), T_d is the discharge time (s), ΔV is working potential window (V), and m is the mass of active material (g). Further, using the charge-discharge curve, the energy density (E, Wh kg^{-1}) and power density (P, kW kg^{-1}) is calculated by using following equations,

$$E = \frac{0.5 \times C_s \times (V_{max} - V_{min})^2}{3.6} \quad (4)$$

$$P = \frac{E \times 3600}{T_d} \quad (5)$$

where, C_s is specific capacitance (F g^{-1}), V_{max} and V_{min} are maximum and minimum potentials during charging and discharging cycles (V) and T_d is discharging time (s).

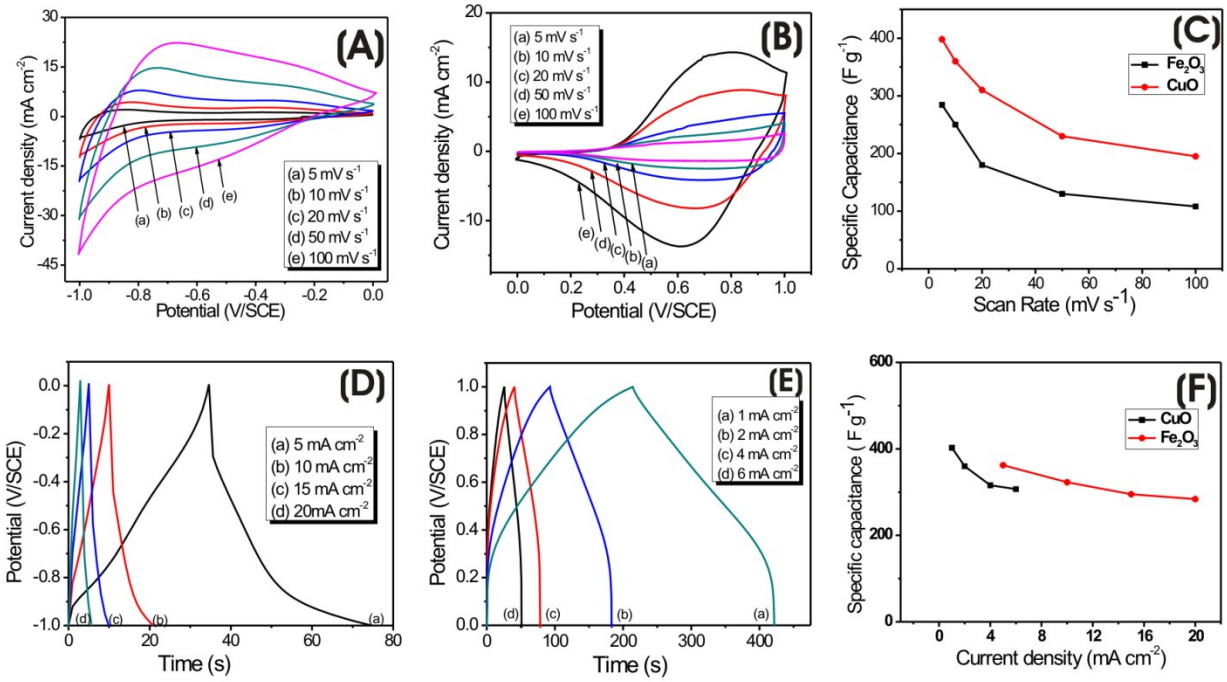

Fig. S3 (A, B) CV curves at various scan rates for Fe_2O_3 and CuO thin films, (C) graph of specific capacitance at various scan rate for Fe_2O_3 and CuO thin films, (D, E) GCD curves at various current densities for Fe_2O_3 and CuO thin films, (F) graph of specific capacitance at various current densities for Fe_2O_3 and CuO thin films.

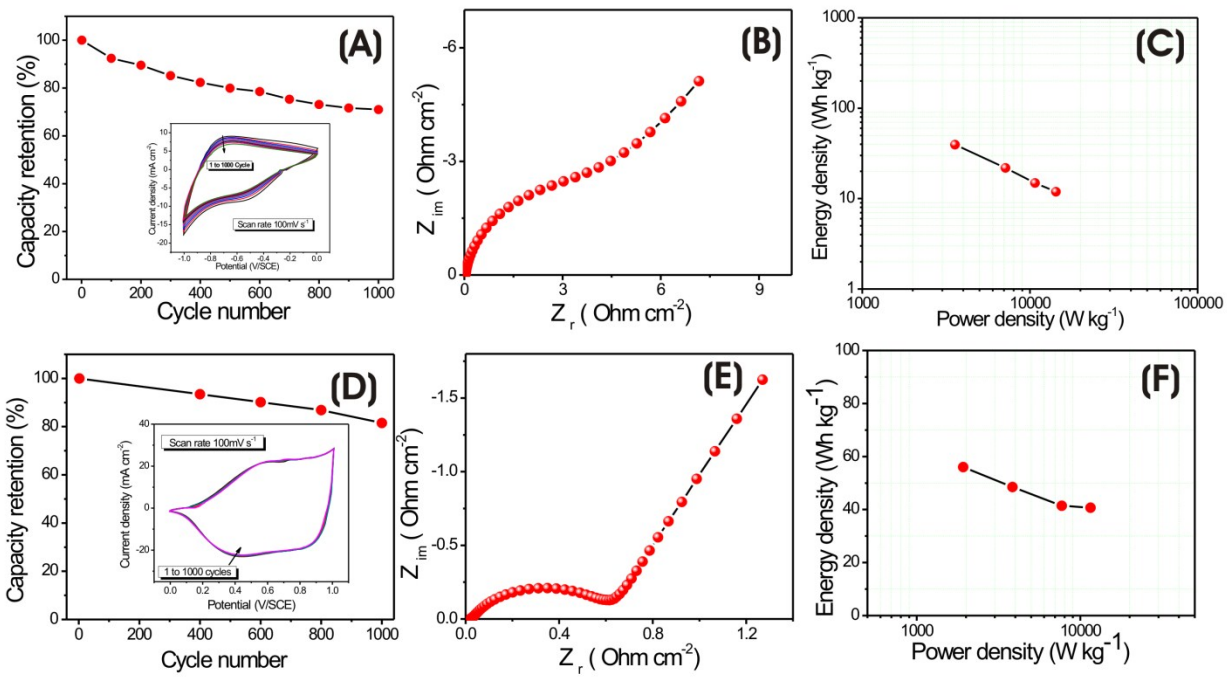

Fig.S4 (A) Graph of capacity retention for various cycle number (inset shows CV curves for various cycle numbers), (B) Nyquist plot, (C) Ragone plot for Fe_2O_3 thin film, (D) graph of capacity retention for various cycle number (inset shows CV curves for various cycle numbers), (E) Nyquist plot and (F) Ragone plot for CuO thin film

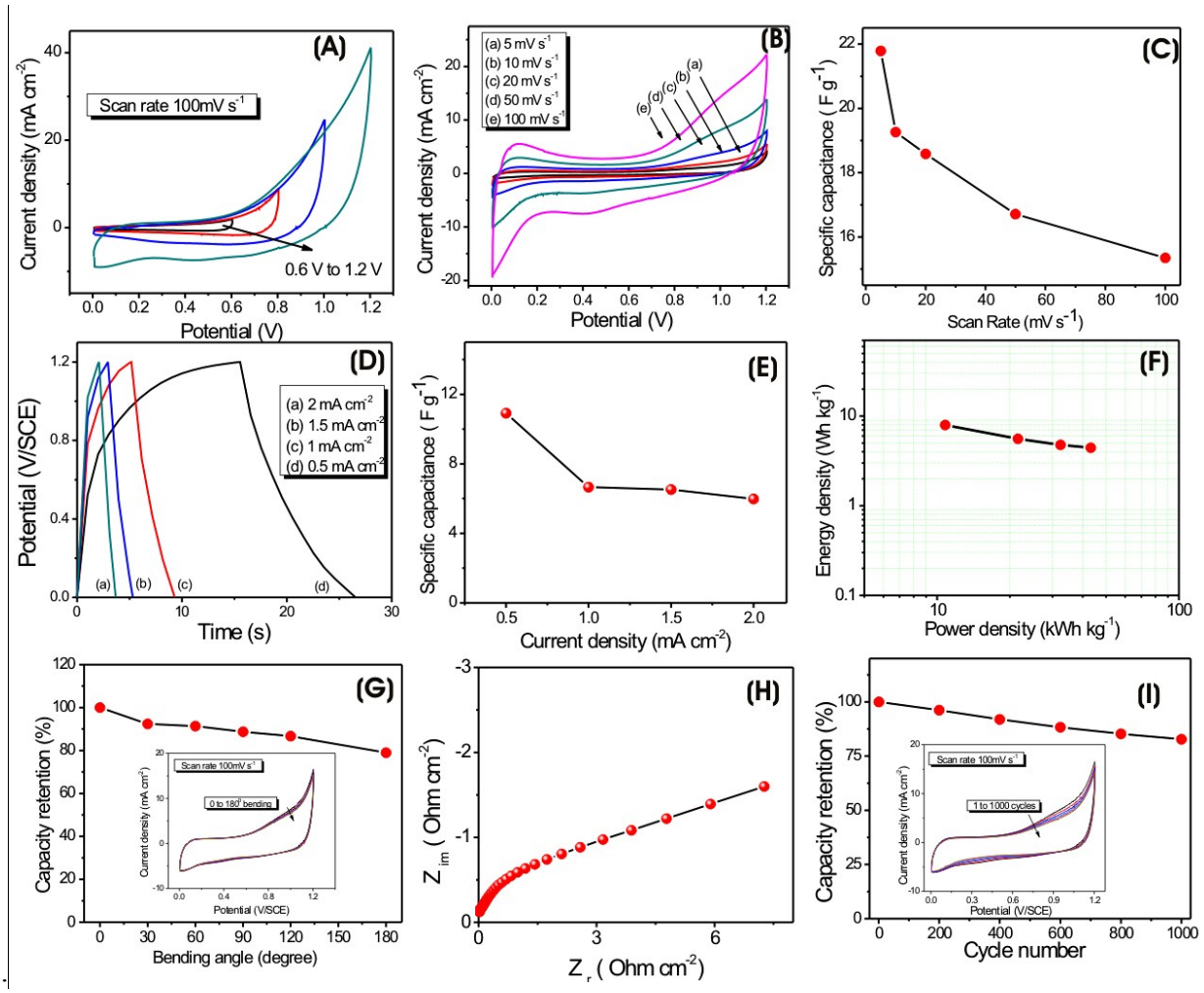

Fig. S5 (A) Window variation (0 to 1.2 V) at scan rate of 100 mV s^{-1}, (B) CV curves at various scan rates, (C) graph of specific capacitance as function of scan rate, (D) GCD curves at various current densities, (E) graph of specific capacitance as a function of current densities, (F) Ragone plot, (G) graph of capacity retention at various bending angles, (inset shows CV curves at various bending angle), (H) Nyquist Plot, (I) graph of capacity retention at various cycle number (inset shows CV curves at various cycle numbers) for Fe_2O_3/Fe_2O_3 symmetric device.

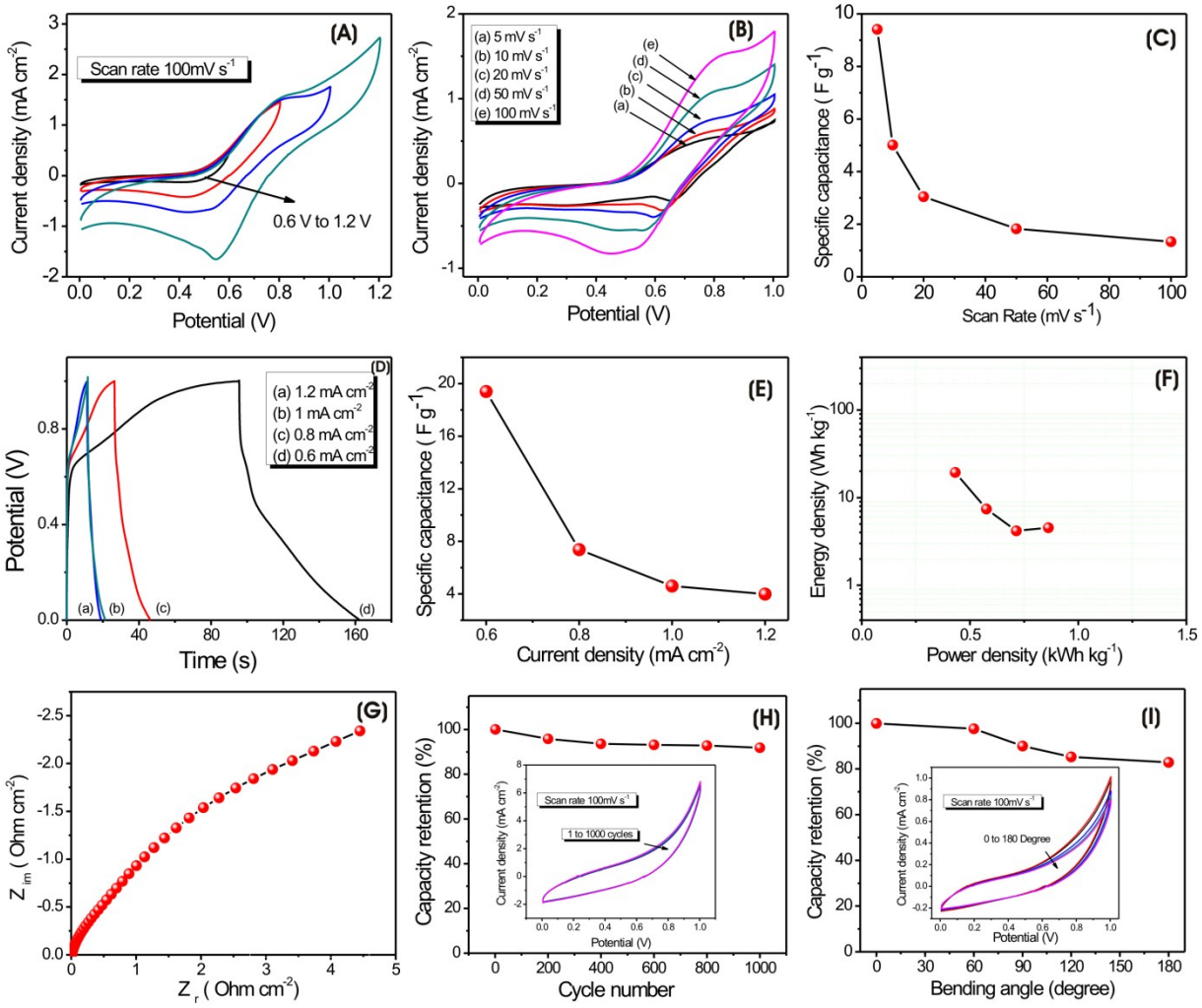

Fig. S6 (A) Window variation (0 to 1.2 V) at scan rate of 100 mV s^{-1}, (B) CV curves at various scan rates, (C) graph of specific capacitance as function of scan rate, (D) GCD curves at various current densities, (E) graph of specific capacitance as a function of current densities, (F) Ragone plot, (G) Nyquist Plot, (H) graph of capacity retention at various cycle number (inset shows CV curves at various cycle numbers) and (I) graph of capacity retention at various bending angle, (inset shows CV curves at various bending angles) for CuO/CuO symmetric device.

References:

[1] P. Kulal, D. Dubal, C. Lokhande, V. Fulari, J. Alloys Compd., 2011, 509, 2567.

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