Supporting Information

Preparation of supercapacitor electrode materials from e-waste: Eco-friendly Cu recovery from printed circuit board waste using reduced graphene oxide and upcycling to Cu/CuO@C

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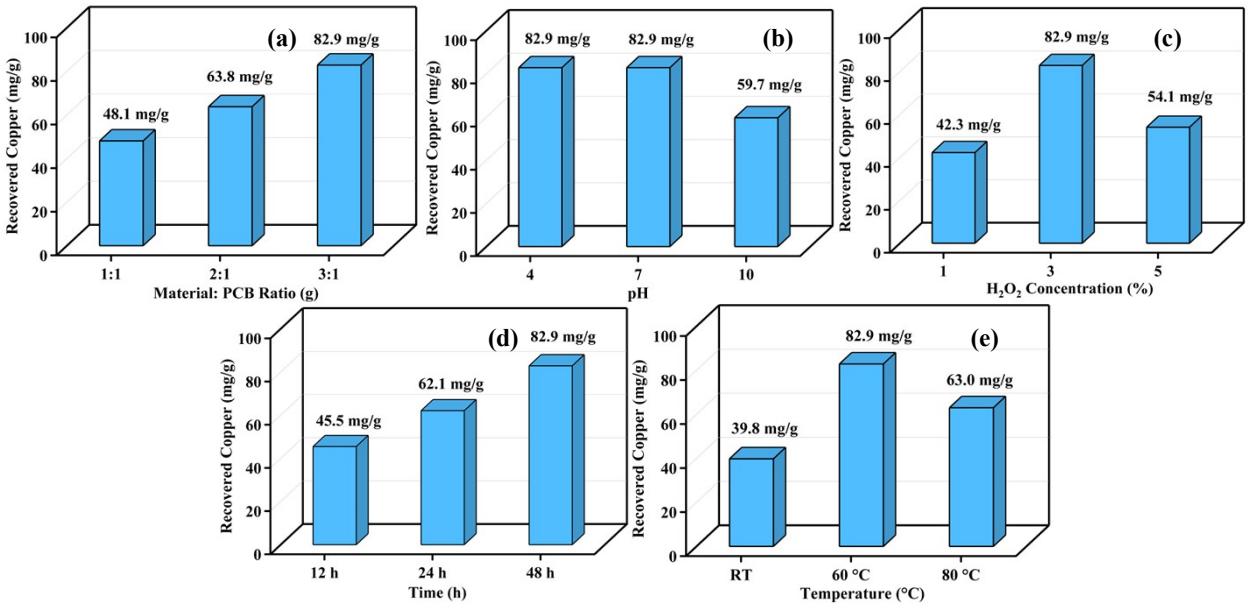


Fig. S1. (a) Effect of Material: WPCB ratio (b) Effect of pH (c) Effect of H_2O_2 Concentration (d) Effect of Time (e) Effect of Temperature.

Effect of ratio: Based on the findings in **Fig. S1a**, the leaching efficiency was evaluated for three different material and WPCB ratios: 1:1, 2:1, and 3:1, under the specific conditions involving a 3-volume percentage of H_2O_2, a temperature of 60 °C, and a leaching duration of 48 hours. The study indicates that the leaching efficiency is higher when the material–WPCB ratio is 3:1. More reduced graphene oxide means more functional oxygenous groups, which means that the leaching efficiency increases as the material ratio increases.

Effect of pH: **Fig S1b** shows the leaching efficiency at three various pHs 4, 7, and 10 in specific conditions, including a 3-volume percentage of H_2O_2, a material – WPCB ratio of 3:1, a leaching experiment duration of 48 hours, and a temperature of 60 °C. The results indicate that pH 4, and 7 yield a higher copper recovery than pH 10. Cu(II) species typically exist as Cu^{2+} below pH 7, as $Cu(OH)^{+}$ and $Cu(OH)_2$ at pH 7, as $Cu(OH)_2$ from pH 8 to 11, and as $Cu(OH)_3^{-}$ and $Cu(OH)_4^{2-}$ above pH 11.[1] In pH 4, and 7 copper leaching efficiency was 100%, higher than pH 10 because H_2O_2 will be unstable at a higher pH.[2]

Effect of H_2O_2 Concentration: In **Fig. S1c**, the correlation between H_2O_2 concentration and leaching efficiency is depicted under specific conditions: an initial pH of 7, a material - WPCB ratio of 3:1, a leaching experiment duration of 48 hours, and a temperature of 60 °C. The leaching experiment was conducted using three different volume percentages of H_2O_2: 1%, 3%, and 5%. The results revealed that the 3% volume of H_2O_2 exhibited higher leaching efficiency than the other two percentages. Through the liberation of oxygen by H_2O_2 decomposition, copper oxide can be formed in WPCBs via the oxidation of the copper metal. At higher concentrations, hydrogen peroxide undergoes decomposition reactions, producing oxygen gas.[3] The liberated gas bubbles may hinder the contact between the leaching solution and the copper source (WPCB), reducing efficiency.

Effect of Time: **Fig. S1d** presents the leaching efficiency of r-GO (reduced Graphene Oxide) at three different periods: 12 hours, 24 hours, and 48 hours, under specific conditions comprising a 3-volume percentage of H_2O_2, a material – WPCB ratio of 3:1, and a temperature of 60 °C. The finding demonstrates that progressive leaching efficiency increases from 12 to 48 hours. Consequently, all leaching experiments were conducted for 48 hours.

Effect of Temperature: In **Fig. S1e**, the leaching efficiency is depicted at three different temperatures: 25 °C, 60 °C, and 80 °C, under specific conditions which include a 3-volume percentage of H_2O_2, a material – WPCB ratio of 3:1, and a time duration of 48 hours. The outcomes indicate that the highest leaching efficiency was observed at 60 °C. At higher temperatures, hydrogen peroxide undergoes decomposition, releasing oxygen gas. This liberated oxygen becomes absorbed on the material's surface, hindering its contact with peroxide. Consequently, at higher temperatures, the efficiency of copper recovery is reduced.[4]

The Cu(I)/Cu(II)/rGO after PCB leaching was stripped with H_2SO_4 to recover Cu as $CuSO_4$. The obtained blue colour solution was evaporated to obtain $CuSO_4$ and analysed by SEM EDAX. As shown below Cu is the only metal present in the recovered $CuSO_4$ indicating the high purity of the recovered Cu. The corresponding SEM EDAX evidence is provided in the supporting information in the revised manuscript as Fig. S2.

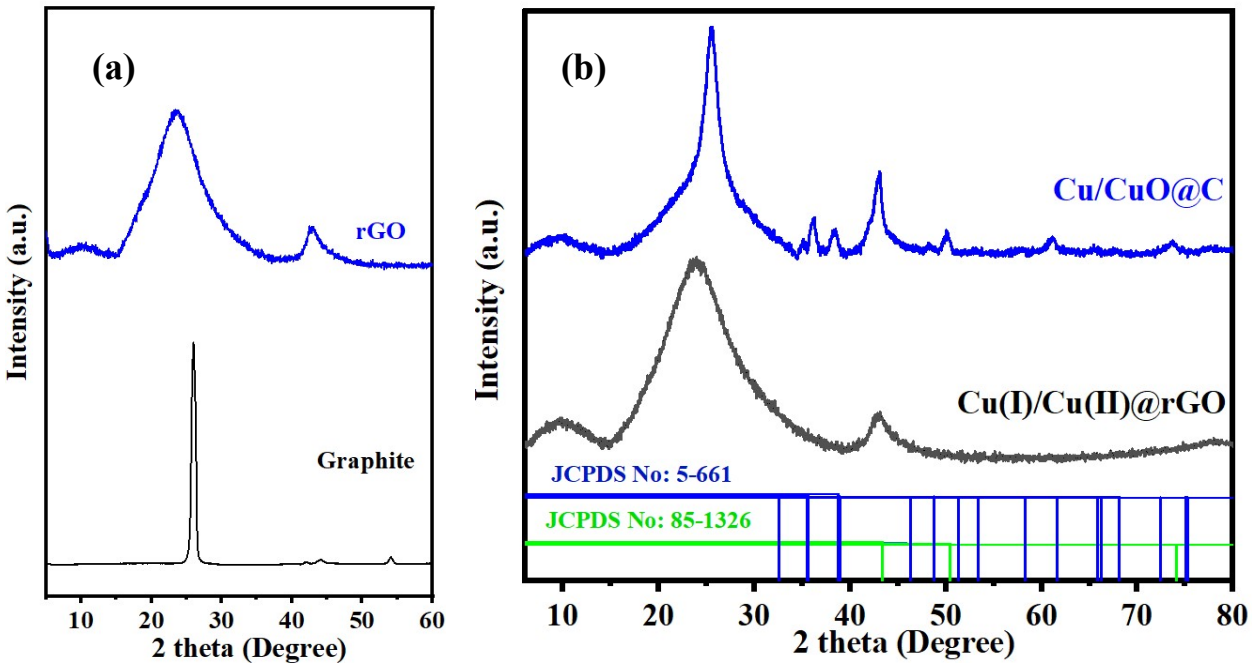


Fig. S2. XRD spectra of (a) Graphite and reduced graphene oxide (rGO) (b) After leaching material (Cu(I)/Cu(II)@rGO) and 500 °C Calcined material (Cu/CuO@C).

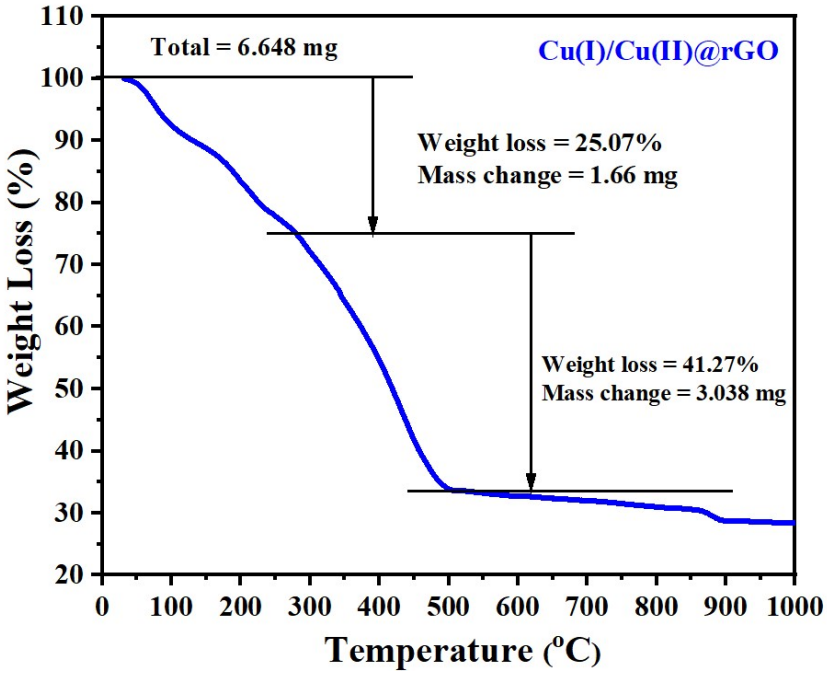


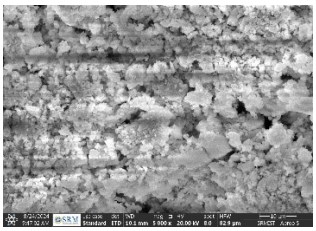
Fig. S3. TGA graph for reduced graphene oxide after leaching (Cu(I)/Cu(II)@rGO).

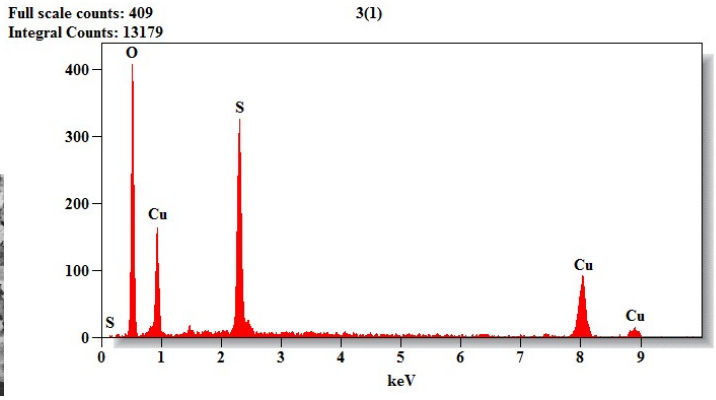
$$rGO - COOH + Cu^{2+} \rightarrow rGO - COO^{-} - Cu^{2+} + H^{+} \quad \text{---------- (1)}$$

$$(rGO - COOH)_2 + Cu^{2+} \rightarrow (rGO - COOH)_2 - Cu^{2+} + 2H^{+} \quad \text{---------- (2)}$$

$$rGO - OH + Cu^{2+} \rightarrow rGO - COO^{-} - Cu^{2+} + H^{+} \quad \text{---------- (3)}$$

$$(rGO - OH)_2 + Cu^{2+} \rightarrow (rGO - O -)_2 - Cu^{2+} + 2H^{+} \quad \text{---------- (4)}$$





Element	Net Counts	Weight %	Atom %	Atom % Error	Formula
O	2362	46.76	72.48	± 1.26	O
S	3617	17.60	13.62	± 0.23	S
Cu	1435	35.64	13.91	± 0.75	Cu
Total		100.00	100.00		

Fig. S4. SEM-EDAX analysis of the recovered $CuSO_4$.

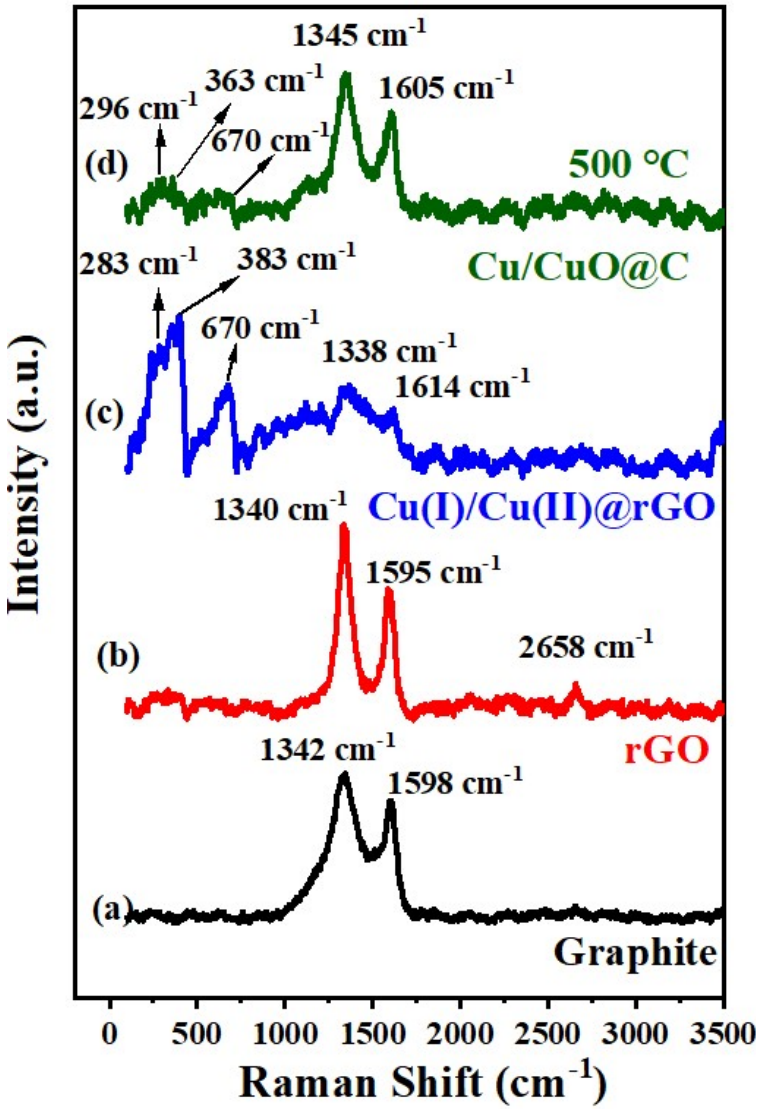


Fig. S5. Raman spectrum for Graphite, reduced Graphene Oxide, and reduced Graphene Oxide after leaching.

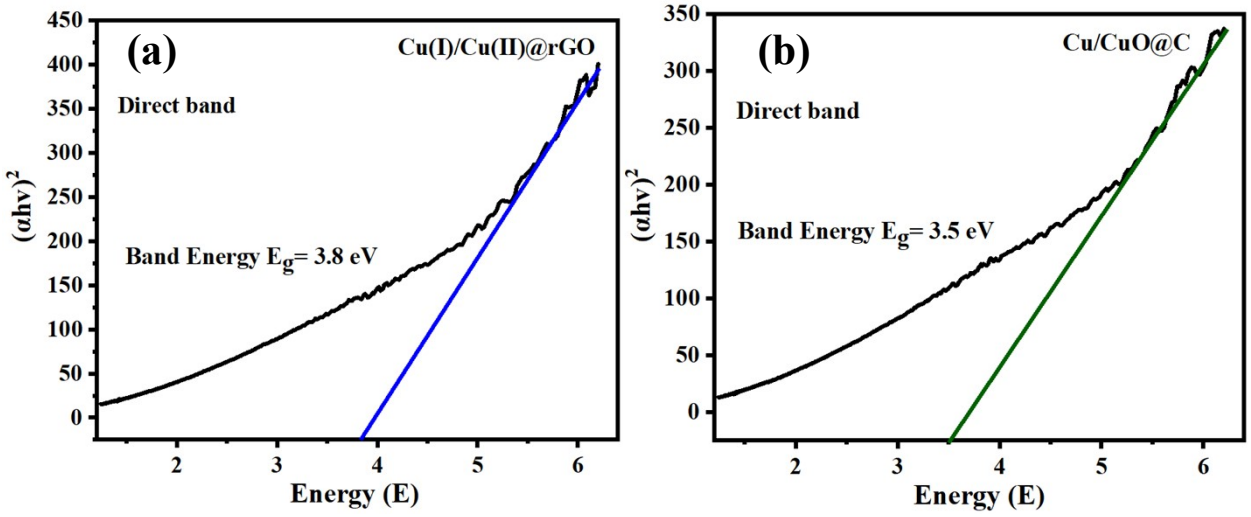


Fig. S6. Bandgap comparison of (a) Cu(I)/Cu(II)@rGO (b) Cu/CuO@C.

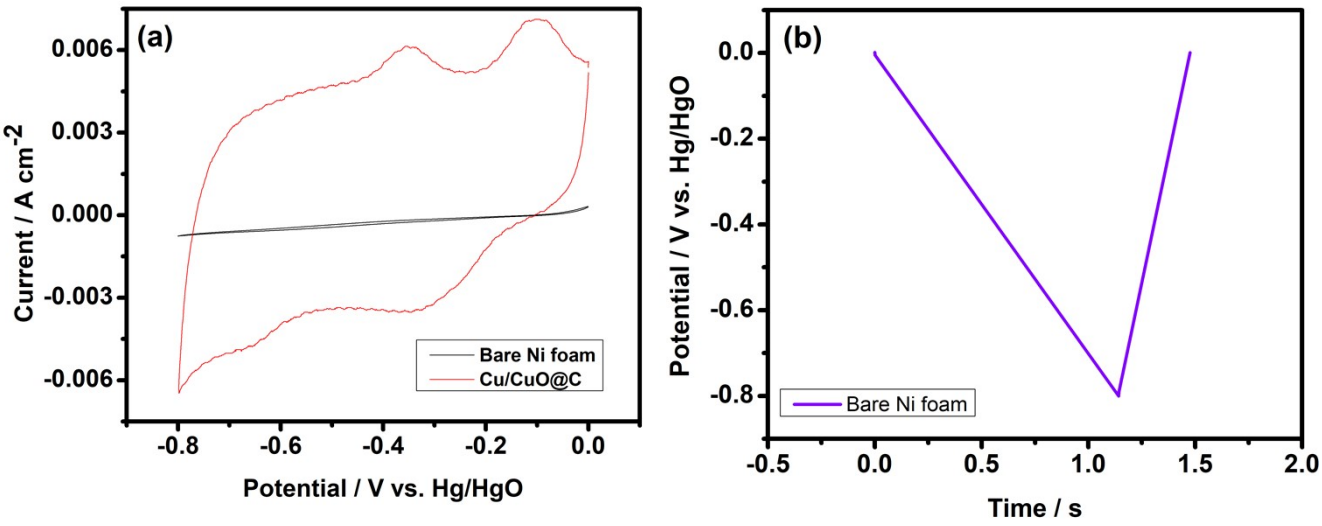


Fig. S7. (a) Comparative CVs of bare Ni foam and that coated with Cu/CuO@C at a scan rate of 10 mV s^{-1}, (b) GCD of bare Ni foam at a specific current of 1 A g^{-1} under similar experimental conditions.

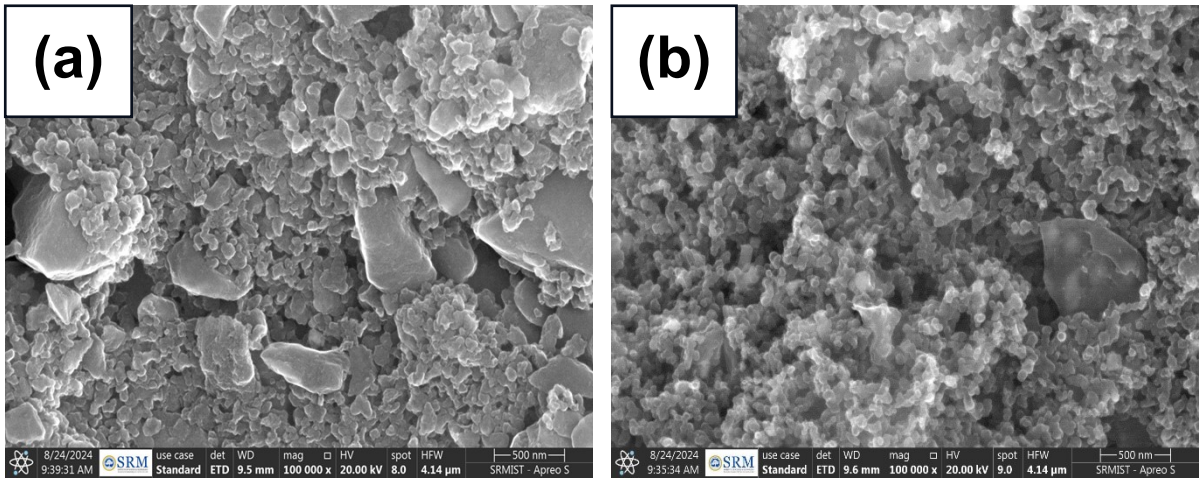
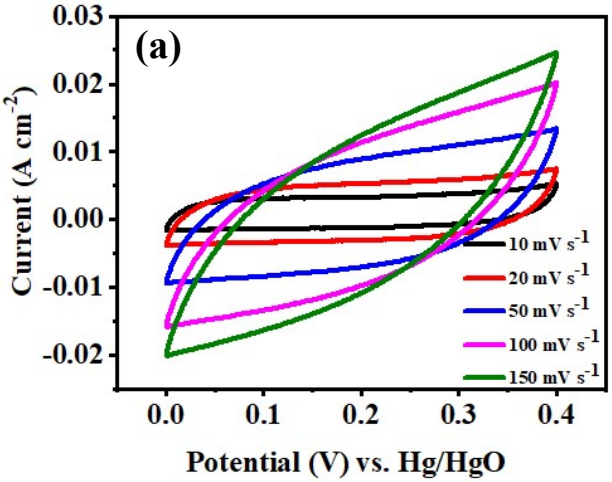


Fig. S8. SEM images of (a) pristine electrode, (b) cycled electrode (after 4000 cycles).


(a)
Current (A cm-2)
Potential (V) vs. Hg/HgO
10 mV s-1
20 mV s-1
50 mV s-1
100 mV s-1
150 mV s-1

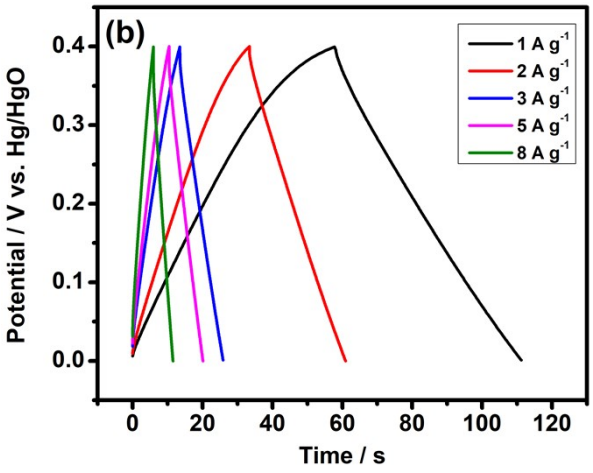

(b)
Potential / V vs. Hg/HgO
Time / s
1 A g-1
2 A g-1
3 A g-1
5 A g-1
8 A g-1

Fig. S9. (a) CV at different scan rates and **(b)** GCD at different specific currents varying from 1 A g^{-1} to 8 A g^{-1} of Activated Carbon in the potential range of 0 to 0.4 V vs Hg/HgO in 1M KOH as electrolyte.

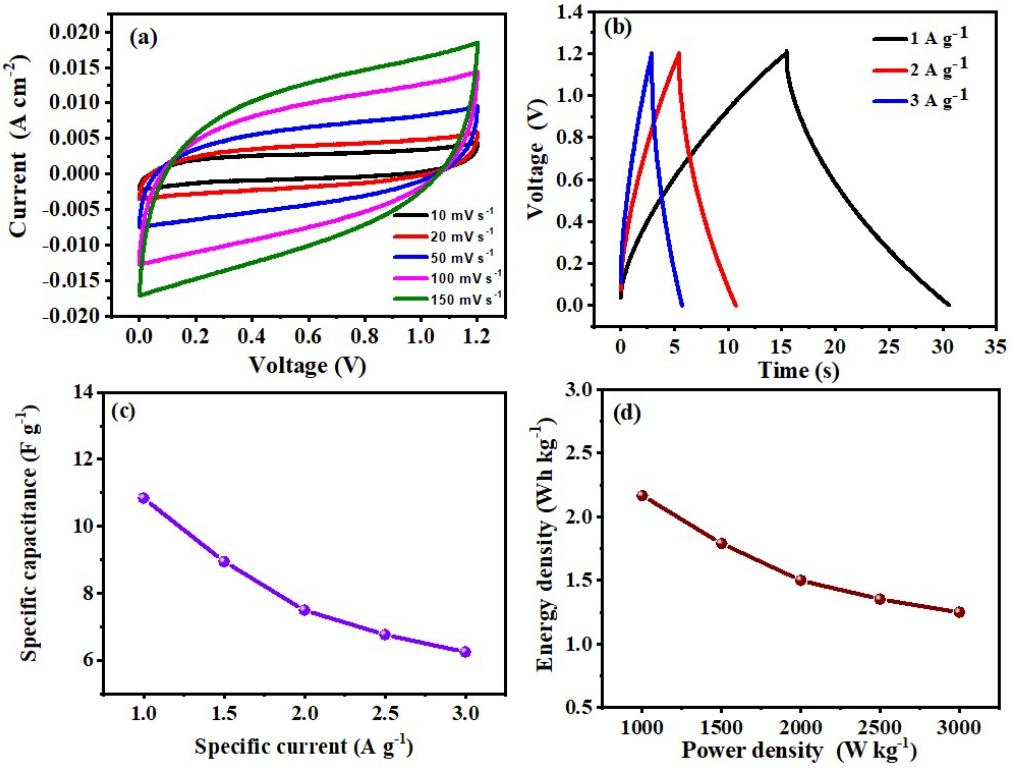


Fig. S10. (a) CV (b) GCD (c) rate capability, (d) Ragone plot of AC||AC symmetric supercapacitor in 1M KOH.

References

1 T. Guo, C. Bulin, Z. Ma, B. Li, Y. Zhang, B. Zhang, R. Xing and X. Ge, *ACS Omega*, 2021, **6**, 16535–16545.

2 A. Hebeish, A. Bayazeed, B. I. A. Gawad, S. K. Basily and S. El-Bazza, *Starch - Stärke*, 1984, **36**, 344–349.

3 M. A. Akuji and D. J. Chambers, *Br J Anaesth*, 2017, **118**, 958–959.

4, Lisińska M, Wojtal T, Saternus M, Willner J, Rzelewska-Piekut M, Nowacki K. 2023, Available at SSRN 4409062.