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Electronic Supplementary Information for:

Substrate-Integrated Core-shell Co₃O₄@Au@CuO Hybrid Nanowires as Efficient Cathode Material for High-performance Asymmetric Supercapacitor with Excellent Cycle Life

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Methods of calculation of capacitance, energy and power densities:

Area capacitance (*Ca*, mF/cm²) is calculated from the Cyclic voltammogram data using the equation:

$$C_a = \frac{\int idt}{a\Delta V},$$

where, i (mA) is the cathodic or anodic current, dt (s) is the time differential, ΔV (V) is the potential window and a (cm²) is the effective area of the individual redox active materials for single electrode measurements. For calculating specific capacitances, area a (cm²) has been replaced with its equivalent mass, m (g), of the active materials only.

From Galvanostatic charge-discharge data, area capacitance (*Ca*, mF/cm²) values are calculated from the discharge data of the electrodes using equation:

$$C_a = \frac{i\Delta t}{a\Delta V}$$
,

where, i (mA) is the discharge current, Δt (s) is the discharge time for discharge window ΔV (V) and a (cm²) is the effective area of the active materials. Here also area a (cm²) has been replaced with an equivalent mass of the active materials, m (g) for calculating specific capacitances.

Volumetric energy (Wh/cm³), equivalent series resistance (ESR) and power densities (*P*, W/cm³) for the fabricated cell are calculated using equations:

$$W = \frac{1}{2 \times 3600} C\Delta V^2$$

$$ESR = \frac{iR_{drop}}{2 \times I}$$
 and $P = \frac{\Delta V^2}{4 \times ESR \times V}$

where, C (volumetric or gravimetric) represents the capacitance of the ASC, ΔV (V) is the discharge voltage, and V (cm³) is the total volume of the assembled cell including electrodes, electrolyte, separator and PET wrapping. However, for calculating Gravimetric energy-power densities, V (cm³) has to be replaced with the total mass (g) of both of the electro-active materials.

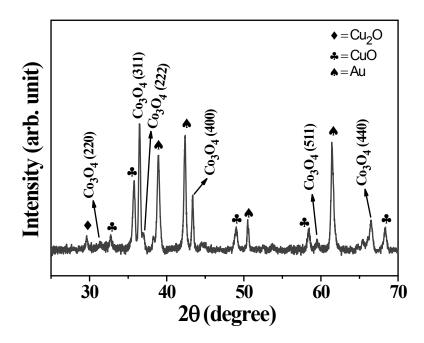


Fig. S1 X-ray diffraction pattern of the as-synthesized Co₃O₄@Au@CuO core-shell NWs.

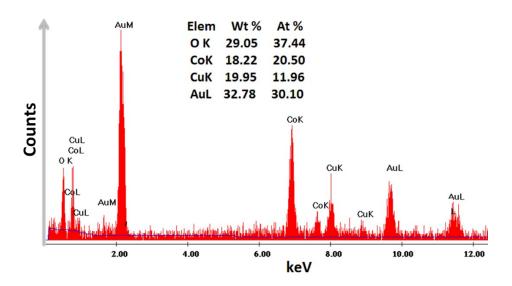


Fig. S2 EDAX pattern recorded for the as-synthesized Co₃O₄@Au@CuO core-shell NWs, showing different constituent materials.

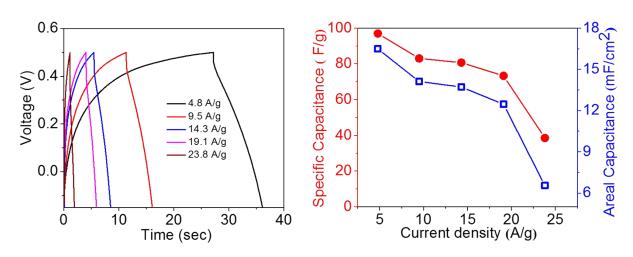


Fig. S3 Galvanostatic charge-discharge curves at different current densities for the Co₃O₄@CuO NW electrode and corresponding capacitance values calculated from the discharge profiles.

Synthesis of nitrogenated $\alpha\text{-Fe}_2O_3$ NRs on carbon cloth (CC) substrate for the negative electrode

Well aligned and vertical arrays of α -Fe₂O₃ NRs were prepared using a modified hydrothermal-route. In brief, 0.15 M FeCl₃. 6H₂O and 1M Na₂SO₄ were mixed in 60 ml distilled water and properly stirred until a clear solution was obtained and no additional HCl was added during the synthesis. The clear solution was then transferred into a Teflon-lined stainless steel autoclave containing a carbon cloth (CC) as substrate for the nucleation and growth of NRs. However, before doing that the CC was copiously cleaned with ultrasonication in miliQ water, followed by washing with water and acetone. The autoclave was then heated at 90°C in a hot air oven for 6 h. Subsequently, the yellow colored CC was taken out from the autoclave and washed copiously with distilled water and acetone followed by drying in an air oven at 60°C overnight. Finally, CC with the yellow colored thin film of iron-oxy hydroxide (FeOOH) was annealed in a tubular furnace at 450°C for 1.5 h under N₂ gas flow to completely convert FeOOH to α -Fe₂O₃. The color of the CC changes from yellow to brick-red in accordance with the formation of α -Fe₂O₃. The mass loading density of those NRs is found to be within the range between 0.35 to 0.42 mg/cm².

The morphology and crystallography of the as-synthesized α -Fe₂O₃ NRs are investigated through FESEM and XRD methods, respectively, as shown in the following figures.

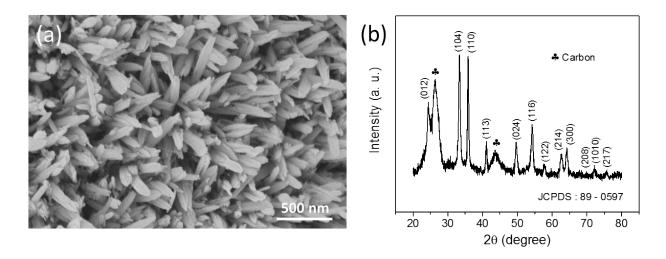


Fig. S4 (a) FESEM image of the high-density vertical arrays of α -Fe₂O₃ NRs grown on the CC substrate. Average length and diameters of the NRs are found to be 550 (± 50) nm and 90 (±10) nm, respectively. The CC substrate is completely covered by the synthesized NRs, suggesting the uniformity of the NR growth. (b) The X-ray diffraction pattern of the α -Fe₂O₃ NRs consists of peaks that can be perfectly indexed with the characteristic diffraction peaks of rhombohedral α-Fe₂O₃ (JCPDS:89-0597), with no trace of any other oxides or hydroxides of iron. However, the carbon related diffraction peaks come from the CC substrate underneath.

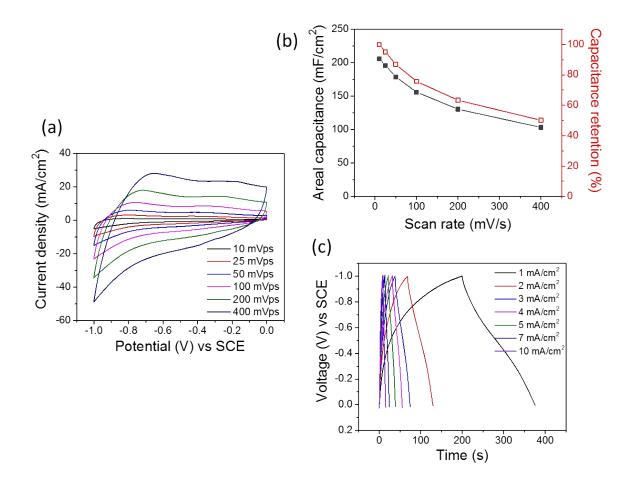


Fig. S5 (a) Cyclic voltammetry (CV) curves of the α -Fe₂O₃ NRs electrode at different potential scan rates with the potential window between 0V and -1V; (b) Variation of areal capacitance and capacitance retention as a function of potential scan rates; and (c) Galvanostatic charge-discharge curves for the α -Fe₂O₃ NRs at different current densities.

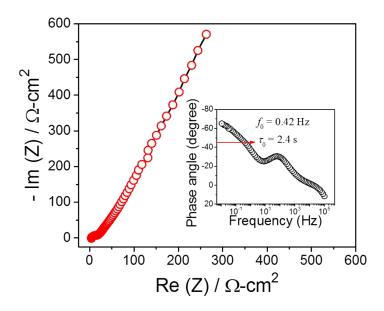


Fig. S6 Nyquist plot for the α -Fe₂O₃//Co₃O₄@Au@CuO hybrid ASC within the frequency range between 10^{-2} Hz to 10^{5} Hz. Inset shows the Bode plot for calculating the response time (τ_0) of the ASC from the frequency at the phase angle of -45°.