Geometrically intricate sheet-on-pillar/flake hierarchy embracing cobaltosic and manganese oxides over flexible carbon scaffold for binder free high energy density supercapacitor

S. Thakur¹, S. Maiti², T. Paul¹, N. Besra³, S. Sarkar³ and K.K. Chattopadhyay^{1, 3, *}

¹ School of Materials Science and Nanotechnology, Jadavpur University, Kolkata 700032, India.
 ² St Thomas College of Engineering & Technology, Kolkata 700023, India
 ³ Departments of Physics, Jadavpur University, Kolkata 700032, India.

*Corresponding author E-mail: <u>kalyan_chattopadhyay@yahoo.com</u>

SUPPORTING INFORMATION:

Characterizations:

The artifact morphology was examined using field emission scanning electron microscope (FESEM, Hitachi S-4800). Crystallinity of the synthesized products was examined by x-ray diffractometer and high-resolution transmission electron microscopy (JEOL JEM-2100). Compositional analysis of the samples was investigated by x-ray photoelectron spectroscopy (XPS) using a SPECS HSA-3500 hemispherical analyzer with a monochromatic Mg K α x-ray source. Raman spectroscopic characterization was performed with WITec alpha 300RA Raman Confocal Microscope with 532 nm diode laser. The Brunauer–Emmett–Teller (BET) surface area of the heterostructures was measured with Quantachrome NovaWin2 Instrument.



Figure S1: SAED pattern of the CMR



Figure S2: Elemental mapping of CMR over a single carbon strand and corresponding EDX spectrum.



Figure S3: XPS spectra of CMR sample.



Figure S4: Pore distribution of CR, CF, CMR and CMF.



Figure S5: CV curves for (a) CR (b) CF (c) CMR electrodes at different scan rates ranging from 5 to100 mV/s; (d) charge–discharge curves of the first 10 cycles for CMF and CMR.



Figure S6: Ragone plots of CF and CR.



Figure S7: Capacitance Retention comparison of CF and CR



Figure S8: First and last 20 cycles of cycle life time of single device.



Figure S9: Specific capacitance of the device from EIS

Plausible Growth mechanism:

In the initial stage of reaction, hydrolysis of urea resulted in gradual release of hydroxyl ions and formation of cobalt hydroxide in solution. With gradual formation of hydroxyl ions, its concentration in the solution rises with the reaction time. As the system reaches a supersaturation level sufficient to overcome the nucleation energy barrier a number of small nuclei forms heterogeneously on the substrate as well as in the solution.¹⁻⁴ Seed layer coated carbon fiber substrate serves as the low energy nucleation site and promotes the growth. From these nucleation centers the nanorods grown via self-assembly. Further oriented attachment of these nanoparticles is favorable for the longitudinal growth of nanopillars. With the alteration of reaction temperature, morphology of the nanoform changed to 2D flake like geometry. With the increment in reaction temperature hydrolysis of urea was resulted more rapidly and saturation level was attained very quickly. As a consequence of such rapid saturation level attainment, nucleation started very quickly. Due to higher reaction rate at elevated temperature, growth started for every point over substrate where the centers remain very close to each other thus acted as extended growth center instead of a point, like the previous case. Again, with high growth temperature, both larger and smaller nucleation happened simultaneously. Among these two, surface energy of larger particles is less compared to smaller ones which favored the aggregation of smaller ones over the larger. Thereafter these nanoforms moved, met and then fused together to form interconnected flake shaped structures.¹⁻⁴

| Sample | Surface Area | Pore Volume | Pore Diameter |
|--------|------------------------|-------------|----------------------|
| | | | |
| CR | 3.13 m ² /g | 0.006 cc/g | 3.602 nm |
| | | | |
| CF | 12.66 m²/g | 0.057 cc/g | 4.076 nm |
| | | - | |
| CMR | 19.04 m²/g | 0.051 cc/g | 4.036 nm |
| | - | - | |
| CMF | 89.56 m²/g | 0.223 cc/g | 4.080 nm |
| | e | e | |

 Table S1⁺: BET parameters of the synthesized nanostructures

| Materials | Specific Energy Density (Whkg ⁻¹) | Specific Power Density (KWKg ⁻ ¹) | Electrolyte | References |
|--|--|--|--------------------------------------|------------|
| Silicon Carbide nano-cauliflowers | 31.43 | 2.5 | 1M Na ₂ SO ₄ | 5 |
| 3D Graphene/MnO ₂ Composite | 6.8 | 0.062 | 0.5M Na ₂ SO ₄ | 6 |
| MoS ₂ /Carbon Cloth | 5.42 | 0.13 | LiCl-PVA Gel | 7 |
| NiS | 9.3 | 0.67 | PVA-LiClO ₄ | 8 |
| VS ₂ /MWCNT's | 42 | 2.8 | PVA- LiClO ₄ | 9 |
| rGO-PMo12 | 17.20 | 0.13 | H ₂ SO ₄ /PVA | 10 |
| Co ₃ O ₄ on Graphene | 80 | 0.5 | PVA/KOH | 11 |
| 2D Co ₃ O ₄ @MnO ₂ nanoflake | 91.9 | 0.8 | PVA-KOH | This Work |

Table S2[†]: Comparison of Energy densities of various symmetric supercapacitor devices

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