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**Supplementary information** 

## Architectural design of hierarchically meso-macroporous carbon for microbial fuel cells anode

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**ES I** Preparation for the Mes-C.

**ES II** Preparation for the DOM-C.

Fig. S1 SEM images of biofilm on the surface (a) and interior (b) of CC after inoculation for 72h.

Fig. S2 CVs of different naked anodes in a PBS solution (50 mM, pH 7.0).

Fig. S3 Voltage output of different anodes MFC.

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## Experimental

## ESI\* Preparation for the Mes-C

8.0 g of Pluronic EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> copolymer (P123), 10 mL of 30 wt% sucrose precursors, 4.8 mL of 0.2 M hydrochloric acid and 10 mL of 50 wt% ethanol solution of SiO<sub>2</sub> were added into the solution under stirring vigorously for 1 h at room temperature. Then the mixture was transferred into Petri dishes and dried at 80°C for 4 h, followed at 150 °C for 6 h. The as-prepared monoliths were scraped from the Petri dishes, and then calcined in a tubular furnace at 900°C at a rate of 5 °C min<sup>-1</sup> for 2 h. The Mes-C-silica nanocomposite was immersed into a 30% HF solution for 72 h to remove silica. The Mes-C was obtained by thoroughly wash with deionized water and subsequent drying.

## ES II \* Preparation for the DOM-C

The SiO<sub>2</sub> colloidal crystal was soaked in a sucrose solution (30 wt %) for 20 min. The sucrose-filled colloidal crystal template was dried at 80°C for 4 h, followed at 150 °C for 6 h. The above infiltration steps were repeated to ensure a complete filling of the void spaces between the silica spheres by sucrose. The sample was carbonized in a tube furnace under N<sub>2</sub> flowing at 900°C for 2 h. The silica spheres were removed using a HF solution to leave behind a surface-tempated 3DOM-C after washing and drying in air at 60°C.

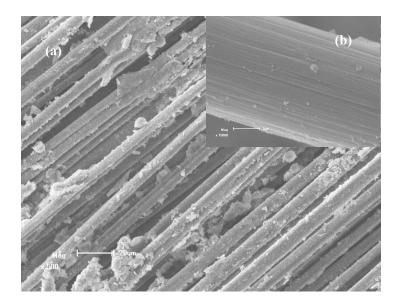


Fig S1

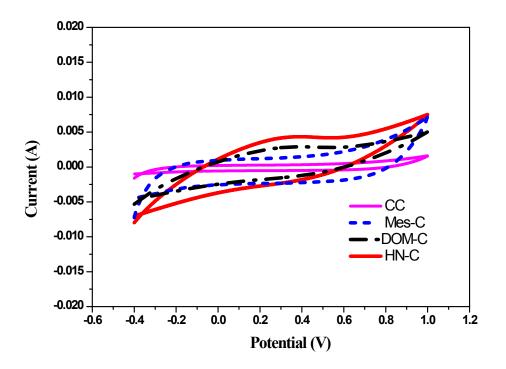


Fig. S2

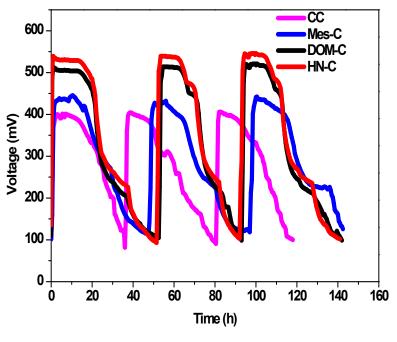


Fig. S3