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## Heterogeneous mesoporous NiCo<sub>2</sub>O<sub>4</sub>-MnO<sub>2</sub>/graphene foam asymmetric supercapacitors with ultrahigh specific energies

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Fig. S1 (a) Digital photograph, (b-d) SEM images of cellular-structured freestanding GF network, (e, f) TEM analysis of GF, (g, h) CNTs grown on GF substrate (CNT/GF) by CVD as the negative electrode in asymmetric supercapacitors, and (i) typical Raman spectra of GF and CNT/GF hybrid.



Fig. S2. EDS line scan analysis of  $NiCo_2O_4$ -MnO<sub>2</sub> core-shell structure.



Fig. S3 (a) nitrogen adsorption/desorption isotherm curve and (b)pore size distribution of NiCo<sub>2</sub>O<sub>4</sub>/GF.



Fig. S4 Nitrogen adsorption/desorption isotherm curve of GF.

Fig. S5a shows the general XPS spectra of NiCo<sub>2</sub>O<sub>4</sub>-MnO<sub>2</sub>/GF composite. The XPS spectrum for Mn 2p (Fig. S5b) has two well-defined peaks separated by ~11.5 eV. They are assigned to the spin-orbit doublets of Mn 2p1/2 (at 653.5 eV) and Mn 2p3/2 (at 641.8 eV). They are characteristic of Mn(IV) oxidation state,<sup>\$1</sup> consistent with the reduction reaction of KMnO<sub>4</sub> mentioned above. The deconvoluted spectra of Co 2p in Fig. S5c also shows two peaks at 779.8 and 794.7 eV assigned to Co<sup>2+</sup> along with two other peaks at 780.6 and 795.8 eV corresponding to Co<sup>3+</sup> as well as two flat satellites at 785.6 and 804 eV.<sup>\$2</sup> Fig. S5d shows the Ni 2p spectra with two Ni<sup>2+</sup> spin-orbit peaks at 854.3 and 871.6 eV and another doublet of Ni<sup>3+</sup> at 855.4 and 872.8 eV. Each doublet was accompanied by a shake-up satellite at 861.2 and 879.5 eV binding energies.<sup>\$3</sup> The deconvoluted C 1s spectra (Fig. S5e) consisted of a sharp peak at 284.4 assigned to the C-C bonds and a small peak at 285.3 eV corresponding to the C-H bonds. The deconvoluted O 1s spectra (Fig. S5f) presented a sharp peak located at 529.7 eV attributed to the O-M bonds, while the shoulder at 531.7 eV is attributed to the surface oxygen defects or adsorbed water on the surface.<sup>\$4</sup>



Fig. S5 (a) The general XPS spectra and deconvoluted high resolution spectra of (b) Mn 2p, (c) Co 2p, (d) Ni 2p, (e) C 1s and (f) O 1s for NiCo<sub>2</sub>O<sub>4</sub>-MnO<sub>2</sub>/GF composite.



Fig. S6 (a) CV curves measured at different scan rates, (b) GCD results and (c) gravimetric and areal capacitances measured at different current densities for the CNT/GF electrode.

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