Electronic Supplementary Material

Urchin-like MgCo₂O₄@PPy core-shell composite grown on Ni foam for a high-performance all-solid-state asymmetric supercapacitor

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S1: Calculation of theoretical specific capacitance of $MgCo_2O_4$ (M= Ni, Zn, Cu, Mn, Mg), theoretical capacitance:

$$C_{S} = \frac{n \times F}{m \times V}$$

Where n= electron number, F= Faraday constant (96485 C mol⁻¹), m= molecular weight, V= redox potential (0.45 V).

For MgCo₂O₄:

$$MgCo_{2}O_{4}+2H_{2}O+e^{-\frac{Charging}{Discharging}}} 2CoOOH+Mg^{+}+2OH$$
$$2CoOOH+2H_{2}O+2e^{-\frac{Charging}{Discharging}}} 2Co(OH)_{2}+2OH^{-}$$

The total number of electrons taking part in the reaction, n=3; m= \sim 206 g mol⁻¹; V= \sim 0.45 V; F= 96485 C mol⁻¹. Substituting the values in equation: C_s= \sim 3122 F g⁻¹.



Fig. S2 FTIR spectra of the urchin-like (a) MC, (b) MCP-2.

Fig. S2 shows the FTIR spectrum for the urchin-like (a) MC, (b) MCP-2 in the range of 400-4000cm⁻¹. The FTIR spectrum of MC reveals some absorption peaks at 577 cm⁻¹, 669cm⁻¹, 883cm⁻¹, 1050cm⁻¹, 1630cm⁻¹, 2890cm⁻¹, 2790cm⁻¹, 3420cm⁻¹. Thereinto, the characteristic bands of MC at 577cm⁻¹, 669cm⁻¹ and 883cm⁻¹ 1050cm⁻¹ are identified as Mg-O (stretching vibration), Mg-O-Mg (bending vibration), Co-O-Co (bending vibration), and Co-O (stretching vibration) bonds, respectively.^{1,2} Specifically, the typical peak of MC at 1630cm⁻¹ is attributed to deviational vibration of liquid H₂O. The broad absorption band of MC at 3420cm⁻¹ corresponds to the stretching vibration of Hydroxyl peak.³ Moreover, the typical peaks of MCP-2 at 2880cm⁻¹ and 2970cm⁻¹ are due to stretching vibration of C-H bond. The band at 1540cm⁻¹ is assigned to the bending vibration of C-N-H in the pyrrole. The typical peak at 1450 cm⁻¹ is assigned to the stretching vibration of C-C bond in pyrrole ring. The peak at 1300 cm⁻¹ is assigned to the =C-H in-plane bending vibration.⁴ The peak at 1170 cm⁻¹ and 1090 cm⁻¹ are assigned to the stretching vibration of C-N bond.^{5,6} The peak at 1040 cm⁻¹ is assigned to the stretching vibration of N-H bond.⁷ The peak at 787 cm⁻¹ further demonstrates the existence of polymerized pyrrole.^{8,9}



Fig. S3 (a) N_2 adsorption-desorption isotherms and (b) pore size distributions of MC, MCP-1, MCP-2 and MCP-3.

Fig. S3 shows the N₂ adsorption–desorption isotherms and pore size distributions of MC, MCP-1, MCP-2 and MCP-3. All the isotherms are categorized as isotherm type IV with H1 hysteresis loops initiated at a very high relative pressure of 0.75. The BET surface areas for MC, MCP-1, MCP-2 and MCP-3 are 37.8, 17.4, 26 and 22.7 m² g⁻¹, respectively (Fig. S3a). Fig. S3b shows the pore size distributions for MC, MCP-1, MCP-2 and MCP-3. The peaks of pore size distribution for MC, MCP-1, MCP-2 and MCP-3 are centered at 3.61, 2.17, 2.65 and 2.62 nm, respectively. These results may be attributed to the penetration of PPy into the pores. The penetrated PPy can act as conducting layer to increase the conductivity of MgCo₂O₄.



Fig. S4 FE-SEM micrographs of the urchin-like (a,b) MCP-1 and (c,d) MCP-3 of different magnification.



Fig. S5 TEM images of the urchin-like (a,b) MCP-1 and (c,d) MCP-3 at different magnification.



Fig. S6 EDX spectrums for the urchin-like (a) MC, (b) MCP-2.

Fig. S6 shows EDX spectrums for the urchin-like (a) MC, (b) MCP-2. Four elements (O, Co, Mg, Au,) can be found from the EDX spectrum of MC. Among them, Au, As conductive agent, is sprayed on the material surface, which can make the material conductive performance better. No other peaks appearing indicates that MC is very pure (Fig. 6Sa). Meanwhile, MCP-2 is the same as it because its EDX spectrum includes six elements of C, N, O, Co, Mg, Au only (Fig. S6b).



Fig. S7 Corresponding elemental mappings of C, N, O, Co, Mg for the urchin-like MCP-2.

Fig. S7 shows mappings for the urchin-like MCP-2. Only five elements (C, N, O, Co, Mg) are found, without any other ones. The result completely corresponds to EDX spectrums for the urchin-like MCP-2.



Fig. S8 The GCD curves of (a) MCP-1, (b) MCP-3, (c) PPy electrodes at different current densities.

Fig. S8 shows the GCD curves of (a) MCP-1, (b) MCP-3, (c) PPy electrodes at the current densities of 1, 2, 3, 5, 10 and 20 A g⁻¹. Moreover, the specific capacitances of MCP-1, MCP-3 and PPy electrodes at the current densities of 1, 2, 3, 5, 10 and 20 A g⁻¹ correspond to 850.7, 927.6, 155.1 (1 A g⁻¹) F g⁻¹; 811.1, 892.4, 122.5 (2 A g⁻¹) F g⁻¹; 781.1, 864, 117.8 (3 A g⁻¹) F g⁻¹; 730.9, 818.8, 106.2 (5 A g⁻¹) F g⁻¹; 655.2, 744.4, 91.6 (10 A g⁻¹) F g⁻¹; 578.5, 653.3, 83.2 (20 A g⁻¹) F g⁻¹.



Fig. S9 Dependence of stored charge vs. sweep rate for MCP-2.

The Trasatti procedure involves analysis of dependence of voltammetric charge as a function of sweep rate. This allows discriminating charge storage due to easily accessible surface (outer) and not easily accessible surface or inner surface. The voltammetric charge (q*) is a measure of total charge exchanged between the electrode and the electrolyte. This includes the amount of OH⁻ diffusing to the inner surface, cracks, pores, grain boundaries etc. As the sweep rate (v $\rightarrow \infty$), all the subsurface regions are excluded and q^* tends to q^*_{outer} where q^*_{outer} is amount of charge stored at outer and easily accessible active surface. On the other hand, as the sweep rate (v \rightarrow 0), the access to subsurface region is fully allowed and q* tends to q*t which is the total charge stored due to whole of active surface including inner and outer surface. The difference between q^*_{total} and q^*_{outer} (q^*_o) gives q^*_{inner} (q^*_i). To calculate the charge storage at $v \rightarrow 0$ and $v \rightarrow \infty$, experiments have been carried out at various scan rates of 2, 10, 20, 50, 80, 100 mV/s with Ohmic drop compensation. The $q_{total}^{*}(q_{t}^{*})$ derived from the intercept of straight $1/q^{*}$ vs. $V^{1/2}$ is 840.34 C g⁻¹ (Fig. S10a). Similarly, q*_{outer} derived from the intercept of q* vs. V^{-1/2} is 453.37 C g⁻¹(Fig. S9b).¹⁰



Fig. S10 (a) Leakage current curves of the all-solid-state device charged at 2 mA to a floating potential of 1.6 V and kept at 1.6 V for 2 h. (b) Self-discharge curves of the device after charging at 1.6 V for 15 min.

For practical application, the leakage current and self-discharge characteristics of the MCP-2 ASC device are also tested, which are not discussed in most of the literatures. In our study, the MCP-2 ASC device is first charged to 1.6 V at 2 mA, then the potential of 1.6 V is kept for 2 h and the current flowing through the supercapacitor is recorded (Fig. S10a). As shown in Fig. S10a, in this constant voltage mode, the current is declining quickly within 15 minutes after the test, then it gradually becomes smaller and more stable later (finally to only 80 µA after 2 h). Such small value of leakage current is ascribed to a few impurities in the electrode material. In addition, the MCP-2 core-shell structure and PVA-KOH gel can prevent potential leakage. Further, Fig. S10b shows the time course of the open-circuit voltage. The device, which is charged at 1.6 V for 15 min later, undergoes rapid self-discharge course in the first two hour and then gradually becomes slow after several hours. Finally, the output voltage of the device reaches to about 0.6 V after 25 h. These studies demonstrate that our devices exhibit low leakage current and excellent selfdischarge characteristics, which is highly desirable for practical applications in electronics.11,12



Fig. S11 Ragone plot of volumetric energy density and volumetric power density of MCP-2//AC

ASC.



Fig. S12 A photograph of two MCP-2//AC ASCs in series.

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