Supporting Information

Graphdiyne Oxide Composite Membrane for Active Electrolyte Enhanced Supercapacitor with super long self-discharge time

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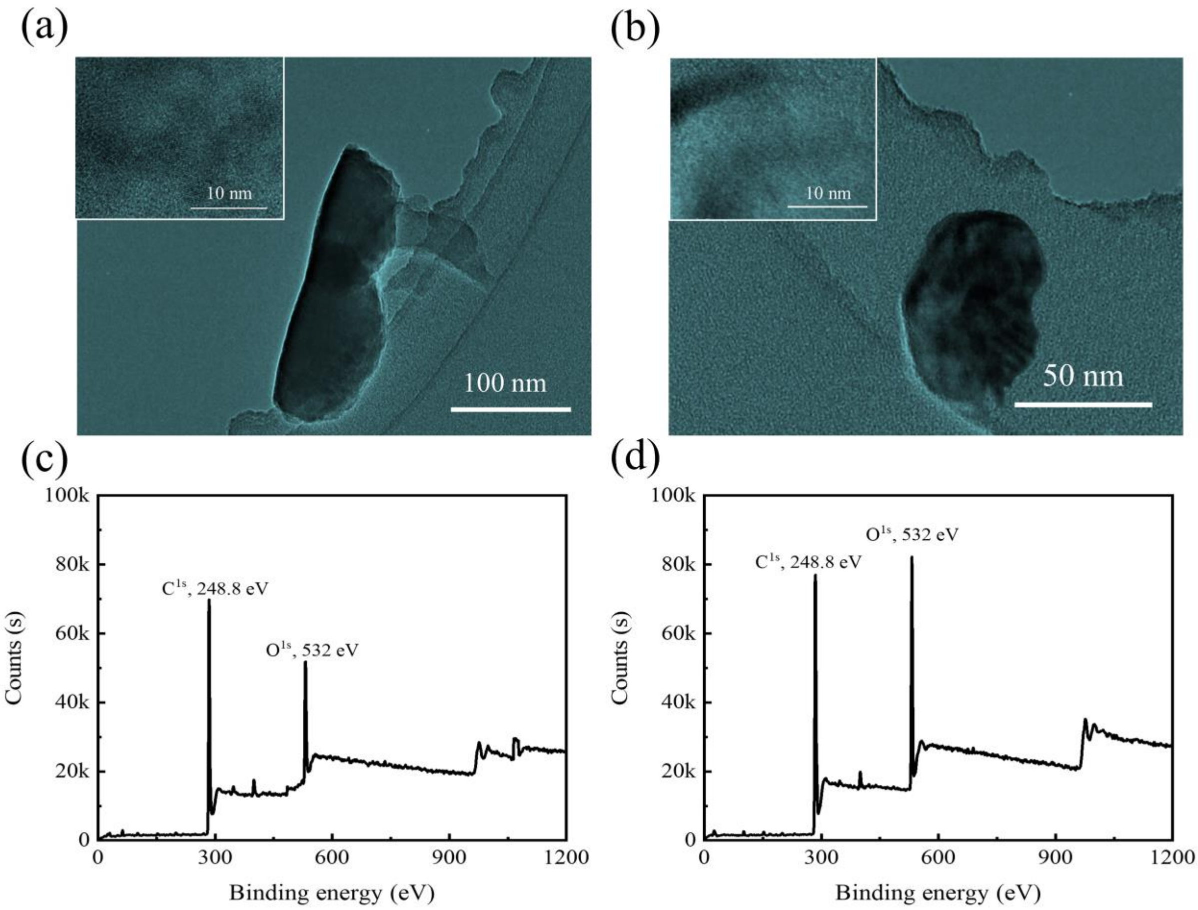

Figure S1 (a, b) TEM and HRTEM images of GDY and GDYO. (c, d) XPS survey scan GDY and GDYO.

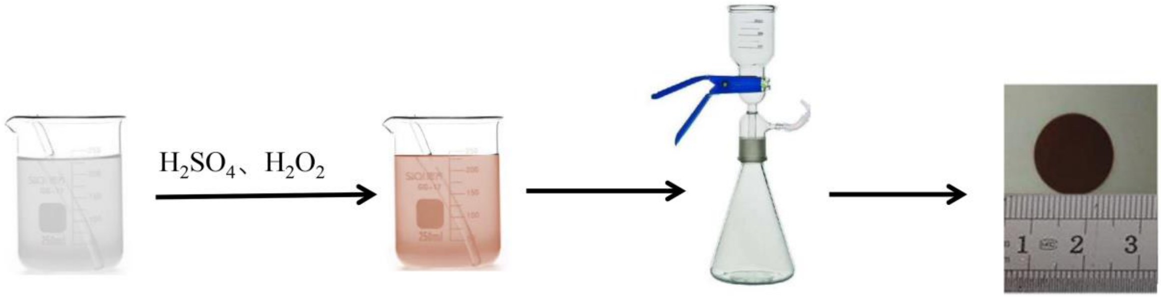

Figure S2 Schematic illustration for the synthesis of GDYO membrane.

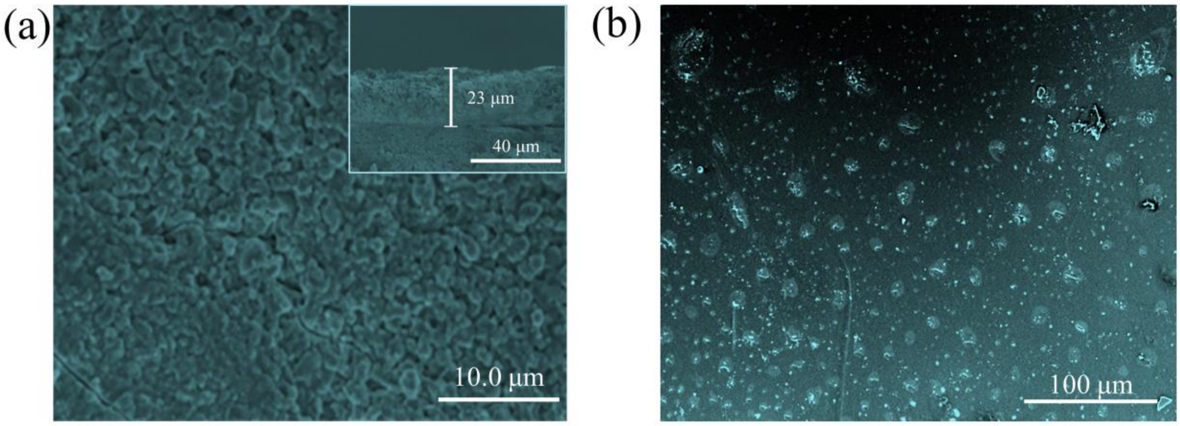

Figure S3 (a)The SEM of GDYO membrane. (b) The SEM of GDYO/PVA-1 membrane.

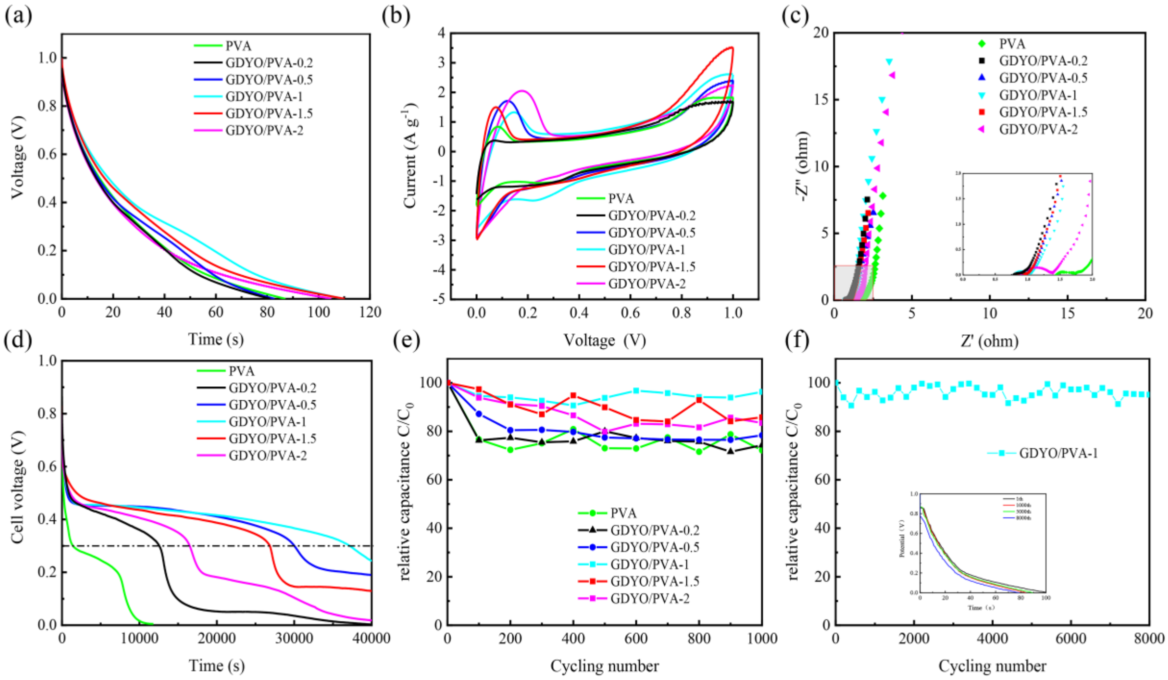

Figure S4 The electrolyte was 1M H_2SO_4 with 0.5M KI added, and the membrane was composed of GDYO composite membranes of different concentrations. (a) Charge–discharge curves of supercapacitor with different membranes at current density 1 A g $^{-1}$. (b) CVs of supercapacitor with different membranes at scan rate of 10 mV s^{-1}. (c) EIS of supercapacitor with different membranes. (d) Self-discharge of the supercapacitors with different membranes. (e) Cycle stability of supercapacitor at current density 1 A g $^{-1}$. (f) Cycle stability of with GDYO/PVA-1 membranes (the illustration is discharge curves at 1, 1000, 5000, and 8000 cycle).

Figure S5 Digital photos of GDY/PVA-1 hydrosol (the illustration is the photo of GDY/PVA-1 membrane)

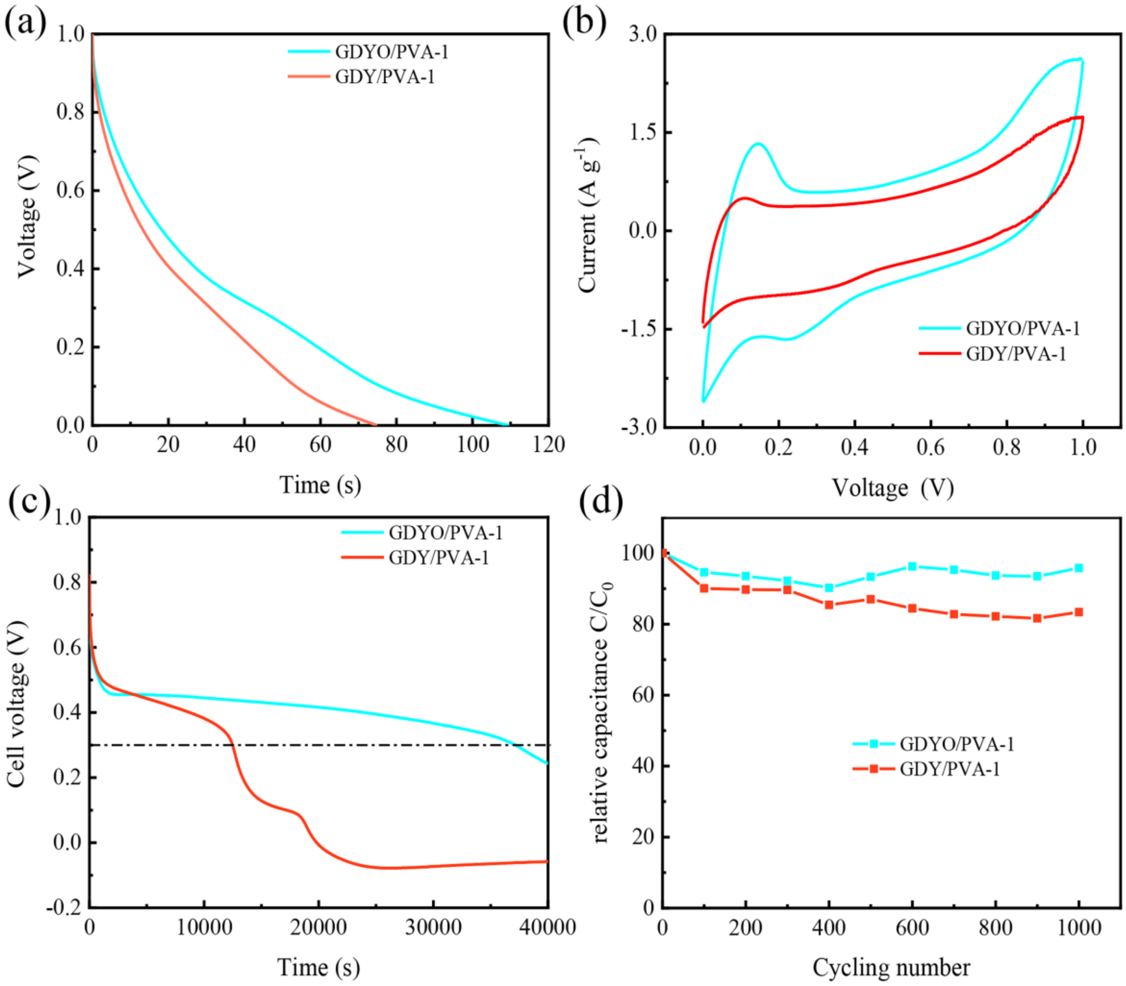

Figure S6 AEESEs based on the different membrane (GDY/PVA-1 membrane and GDYO/PVA-1 membrane) when the electrolyte is 1 M H_2SO_4 and 0.5 M KI mixture (a) Charge–discharge curves at current density 1 A g^{-1}. (b) CVs at scan rate of 10 mV s^{-1}. (c) SDC of the supercapacitors. (d) Cycling stability at current density 1 A g^{-1}.

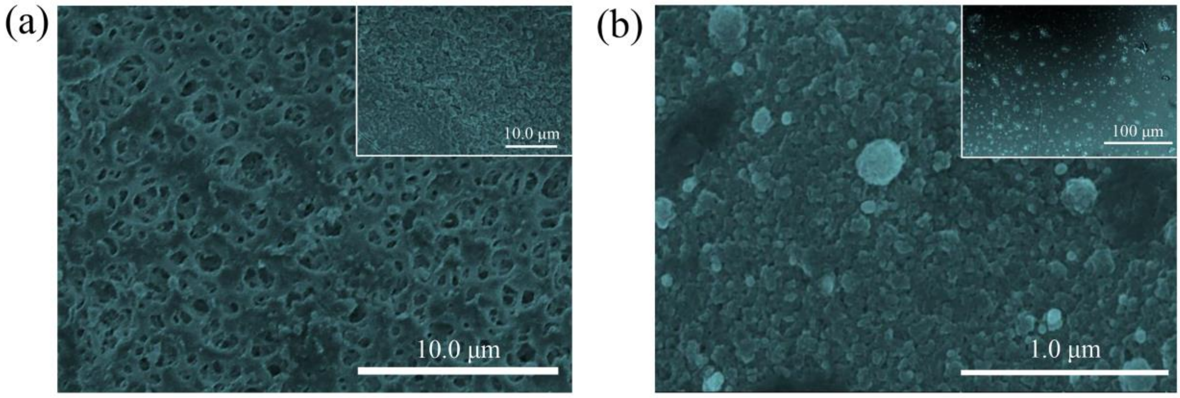

Figure S7 (a) SEM images of GDYO membrane after charge-discharge cycle (the illustration is the SEM image of GDYO membrane before the test). (b) SEM images of GDYO/PVA membrane after charge-discharge cycle (the illustration is the SEM image of GDYO/PVA membrane before the test).

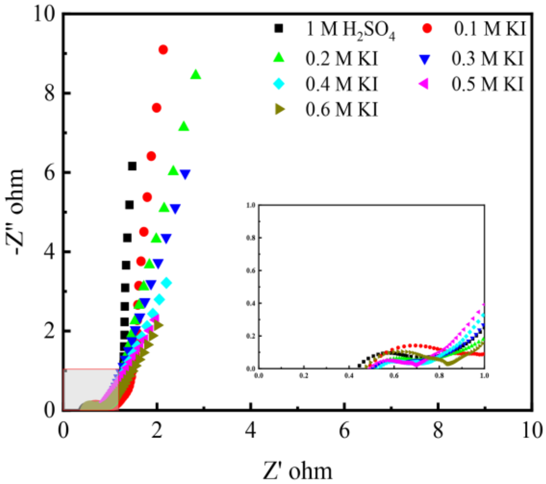

Figure S8 EIS of supercapacitor with different electrolytes.

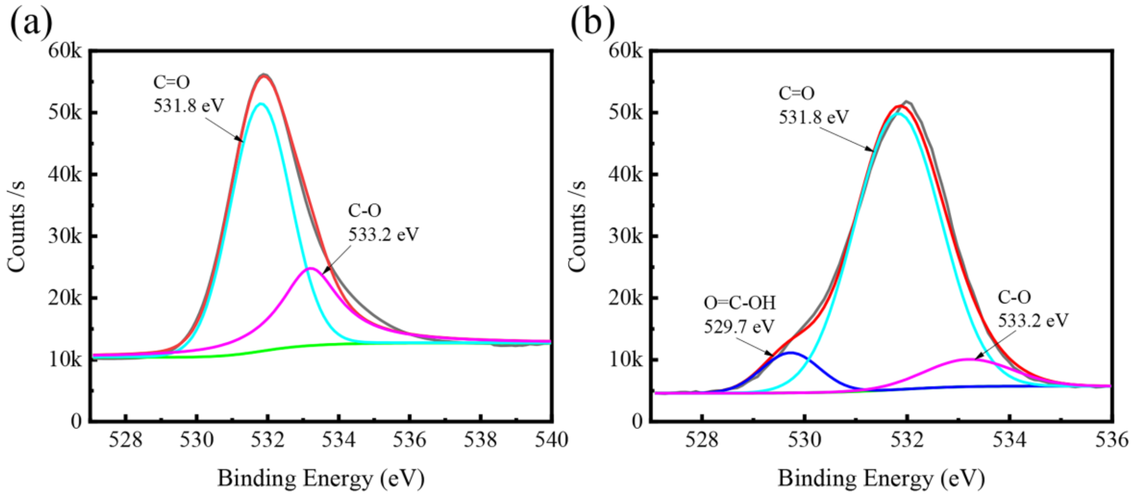

Figure S9 O 1s spectra of (a) GDY and (b) GDYO powder.

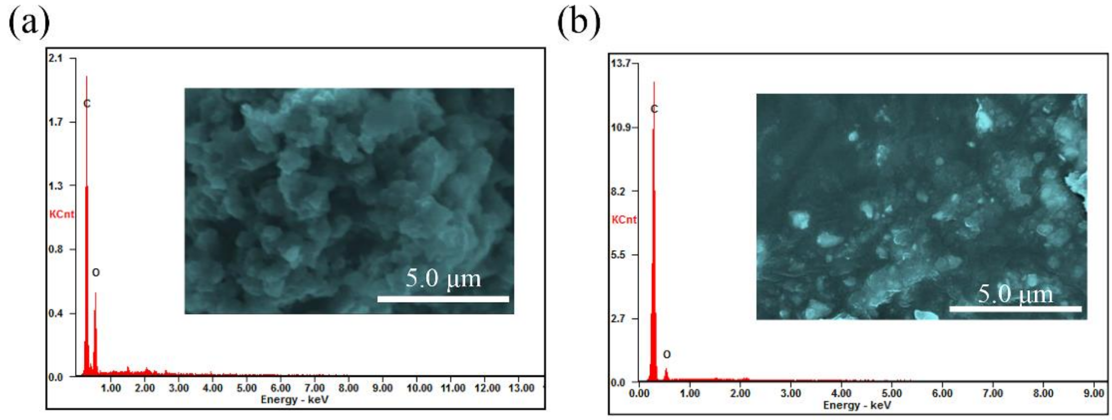

Figure S10 EDS profile and the inset is the SEM photographs of the (a) GDYO membrane. (b) GDYO/PVA membrane.

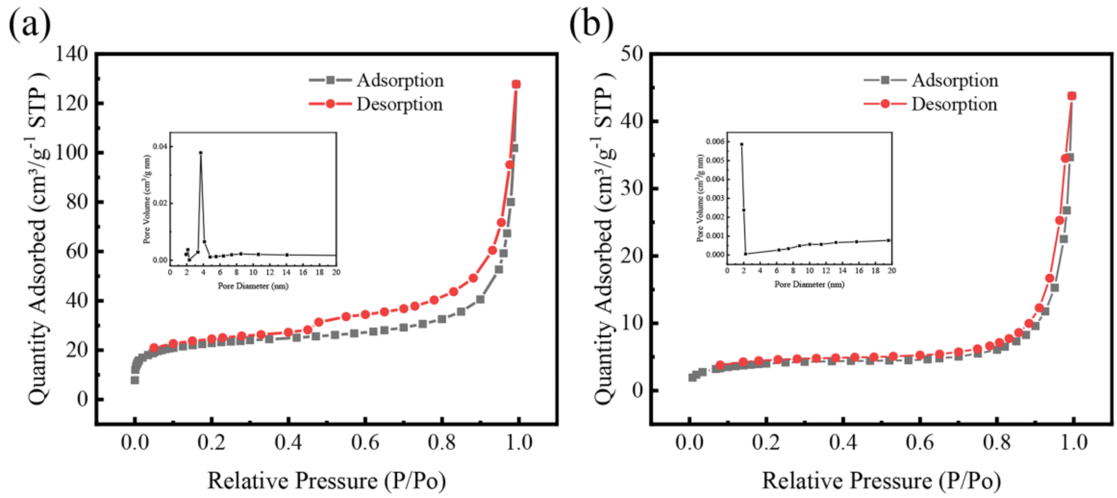

Figure S11 Nitrogen adsorption-desorption isotherms and pore size distribution of the (a) GDY and (b) GDYO

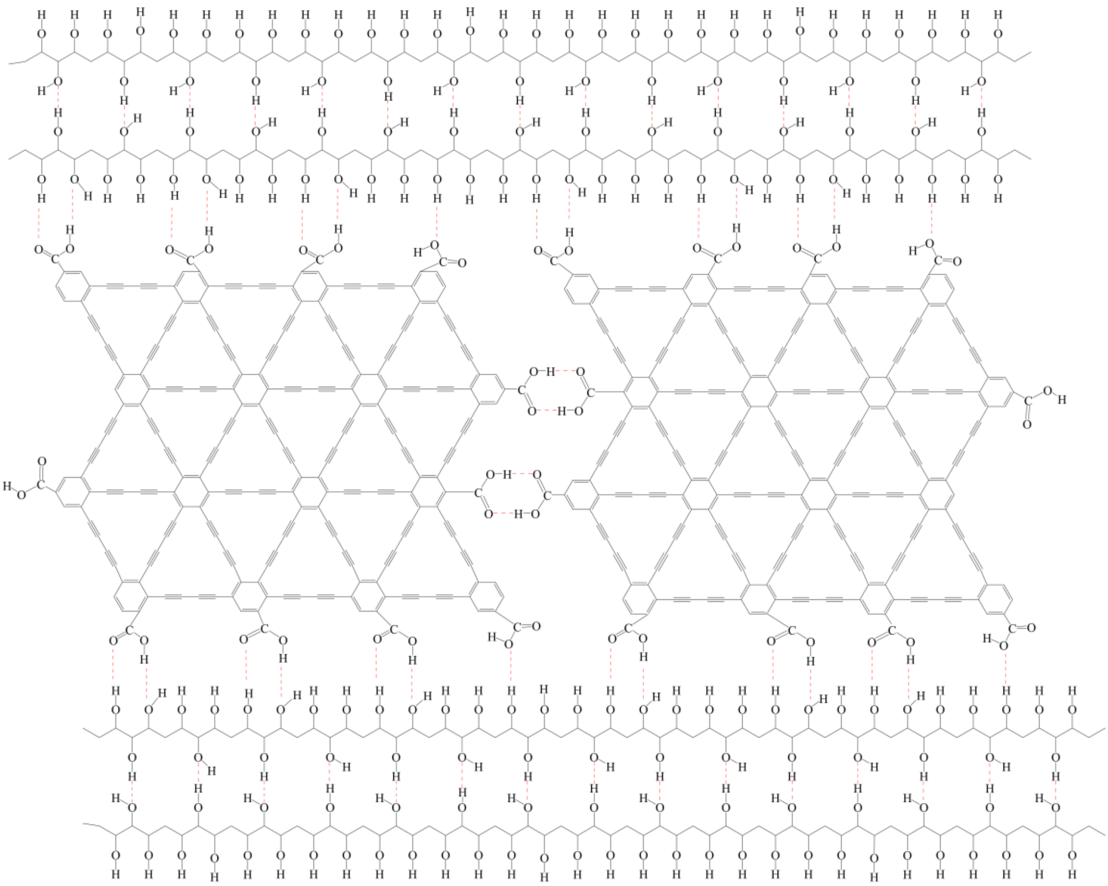

Figure S12 Schematic diagram of GDYO/PVA hydrogen bonding

Table S1 Membrane thickness, water uptake, and proton conductivity of the membranes containing.

Sample	Membrane thickness / mm	Water uptake / %	Proton conductivity / 10^{-2} S cm^{-1}
PP	0.1	98	4.2
GDYO	0.123	85	5.6
GDYO/PVA	0.077	73	3.4

The thickness of the membrane is measured by a helical micrometer

Table S2 Electrical properties of GDYO composite membranes with different concentrations

Sample	Specific capacitance ($F\ g^{-1}$)	Retention capability	self-discharge (s, 1 V−0.3 V)	R_s (Ω)	R_{ct} (Ω)
PP	327.4	68.5 % after 1000 cycles	241.5	0.48	0.11
GDYO	348.9	74.8 % after 1000 cycles	27150	0.41	0.17
PVA	223.5	72.2 % after 1000 cycles	7100	1.43	0.15
GDYO/PVA-0.2	230.6	74.3 % after 1000 cycles	12580	0.79	0.06
GDYO/PVA-0.5	231.7	78.4 % after 1000 cycles	30020	0.83	0.07
GDYO/PVA-1	325.6	96.2 % after 1000 cycles 95.1 % after 8000 cycles	37160	0.79	0.11
GDYO/PVA-1.5	271.3	85.8 % after 1000 cycles	26860	0.85	0.07
GDYO/PVA-2	253.6	83.5 % after 1000 cycles	16500	0.92	0.23

Table S3 Comparison of specific capacitance, self-discharge and retention capability with different reported values

Electrode	Separator	Electrolyte	Specific capacitance ($F\ g^{-1}$)	self-discharge (s, 1 V−0.3 V)	Retention capability	Ref.
GHG	Nafion® 117	H_2SO_4 + HQ	C_c 75.0@ 2.1 A g^{-1}	4686		[1]
GHG	cellulose acetate	H_2SO_4 + HQ	C_c 100.2 @1.3 A g^{-1}	1462		[1]
GHG	cellulose acetate	$CuSO_4$+H_2SO_4	C_c 113 @ 2.1 A g^{-1}	7727		[1]
MXene	Celgard 3501	H_2SO_4 + KI	C_c 166 @ 1.0 A g^{-1}		100% after 5000 cycles	[2]
MWCNTs	glassy fibrous	H_2SO_4+indigo carmine	C_{sp} 50 @ 0.88 mA cm^{-2}		70% after 5000 cycles	[3]
AC	polypropylene sheet	H_2SO_4+ KI	C_{sp} 912 @ 2.0 mA cm^{-2}	1800		[4]
AC	Glass microfiber	H_2SO_4+ KI	C_{sp} 235 @ 1.0 A g^{-1}	25200		[5]
NPS-800	Swagelok®cells	H_2SO_4 + KI	C_c 70 @ 0.7 A g^{-1}		86.2% after 5000 cycles	[6]
AC	GDYO/PVA	H_2SO_4 + KI	C_{sp} 325.6 @1.0 A g^{-1}	37160	96.2 % after 1000 cycles 95.1% after 8000 cycles	This work
AC	GDYO	H_2SO_4 + KI	C_{sp} 348.9@1.0 A g^{-1}	27150	74.8% after 1000 cycles	This work

GHG: graphene hydrogel
MXene: $Ti_3C_2T_x$
AC: Activated carbon

References

1 L. Chen, H. Bai, Z. Huang, L. Li, *Energy Environ. Sci.*, 2014, 7, 1750.
2 J. Fu, L. Li, D. Lee, J. M. Yun, B. K. Ryu, K. H. Kim, *Appl. Surf. Sci.*, 2020, 504, 144250.
3 S. Roldán, Z. González, C. Blanco, M. Granda, R. Menéndez, R. Santamaría, *Electrochim. Acta.*, 2011, 56, 3401.
4 S. T. Senthilkumar, R. K. Selvan, Y. S. Lee, J. S. Melo, *J. Mater. Chem. A.*, 2013, 1, 1086.
5 M. Meller, J. Menzel, K. Fic, D. Gastol, E. Frackowiak, *Solid State Ionics.*, 2014, 265, 61.
6 K. Jayaramulu, D. P. Dubal, B. Nagar, V. Ranc, O. Tomanec, M. Petr, K. K. R. Datta, R. Zboril, P. Gomez-Romero, R. A. Fischer, *Adv Mater.*, 2018, 30, e1705789.