Electronic Supplementary Material (ESI) for Dalton Transactions.


# Supporting Information

## Wrinkled two-dimensional ultrathin Cu(II)-porphyrin framework nanosheets hybridizing with polypyrrole for flexible all-solid-state supercapacitors

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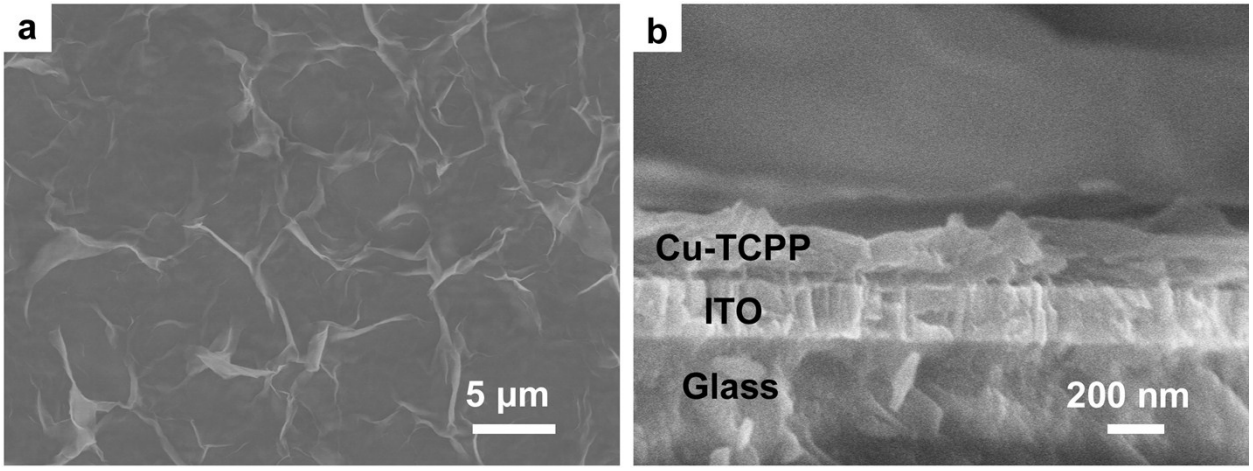


**Fig. S1** SEM images of the flat ultrathin 2D Cu-TCPP film through the electrophoretic deposition of the flat ultrathin 2D Cu-TCPP nanosheets onto the surface of ITO-coated glass for 30 s. (a) The top-view SEM image. There are no macroporous structure existing in the film. (b) The cross-sectional SEM image. It shows that the flat ultrathin Cu-TCPP nanosheets tightly stack.

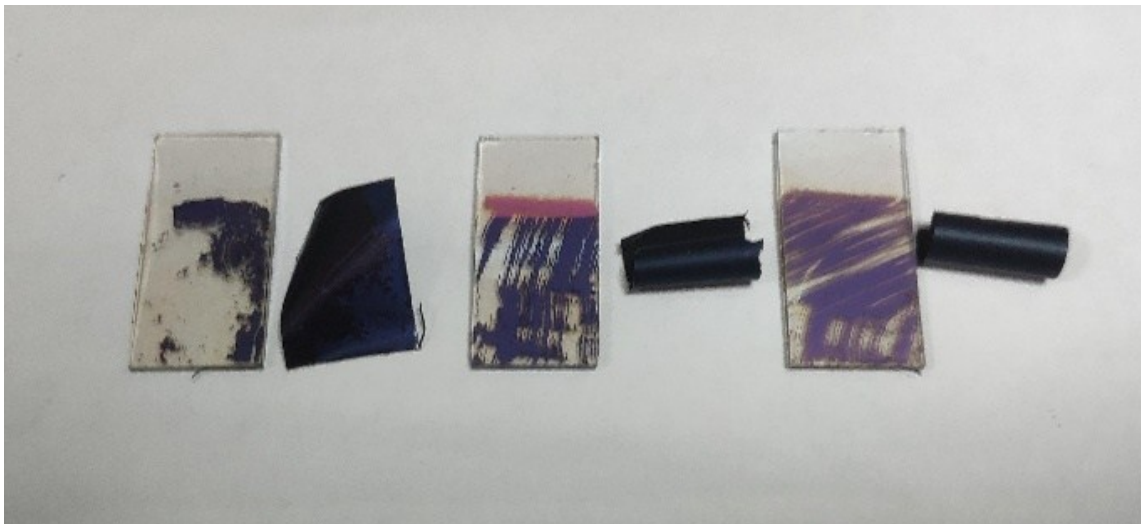

**Fig. S2** Optical photographs of Cu-TCPP/PPy samples prepared through the electrochemical polymerization of PPy with the flat ultrathin Cu-TCPP film on the surface of ITO glass (The electrophoretic deposition time of Cu-TCPP is 30 s, 1 min and 3 min, respectively, from left to right.). It shows that the flat ultrathin Cu-TCPP nanosheets can't completely combine with PPy, which is mainly attributed to that the dense stacking of flat ultrathin Cu-TCPP nanosheets prevents the immersion of pyrrole molecules into the interlayer intervals.

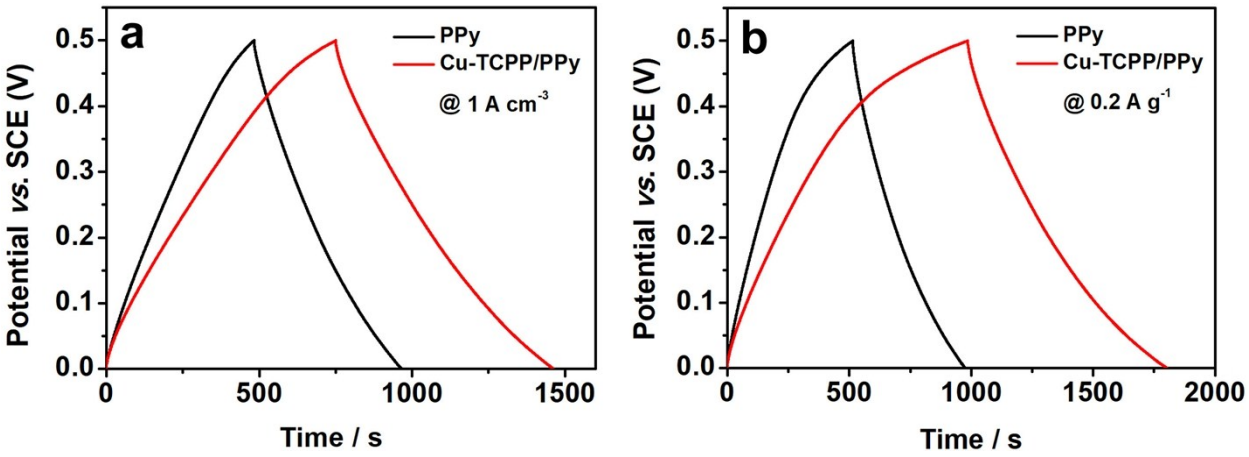


**Fig. S3** GCD curves of Cu-TCPP/PPy (The electrophoretic deposition time of Cu-TCPP is 30 s. The Electrochemical polymerization time is 600 s.) and PPy films at a current density of 1 mA $cm^{-3}$ (a) and 0.2 A $g^{-1}$ (b).

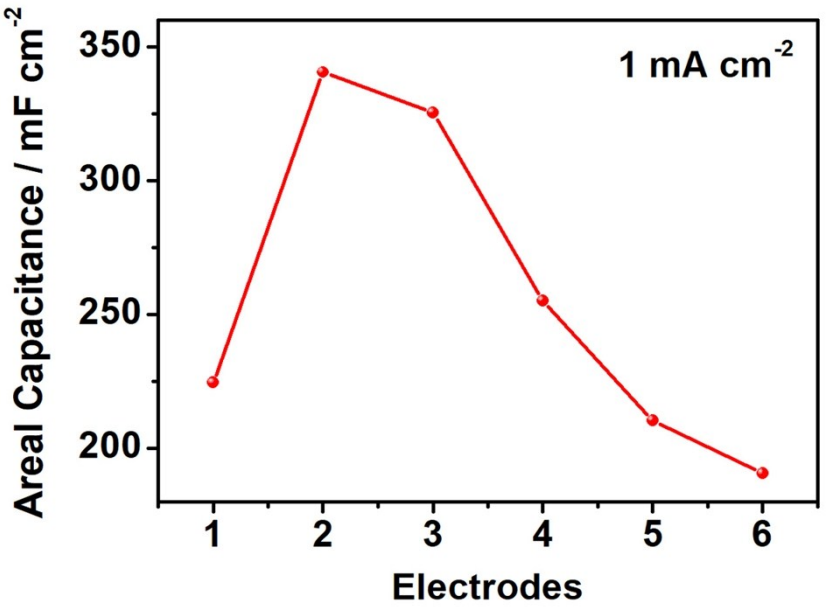


**Fig. S4** Areal capacitance of different Cu-TCPP/PPy electrodes through the electrophoretic deposition of wrinkled ultrathin 2D Cu-TCPP nanosheets for a certain time of 0 s (1), 30 s (2), 1 min (3), 3 min (4), 5 min (5) and 10 min (6) and electrochemical polymerization of PPy at 0.8 V versus Ag/AgCl for 600 s. Current density: 1 mA $cm^{-2}$.

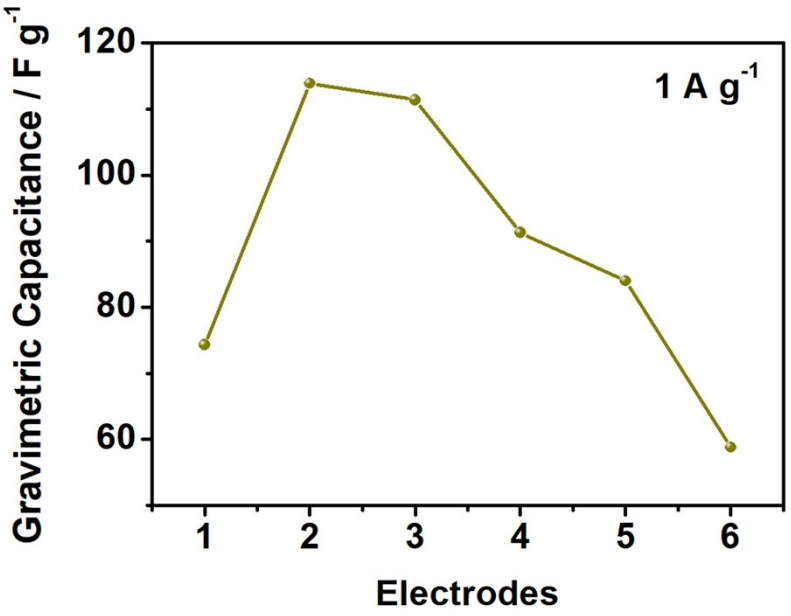


**Fig. S5** Gravimetric capacitance of different Cu-TCPP/PPy electrodes through the electrophoretic deposition of wrinkled ultrathin 2D Cu-TCPP nanosheets for a certain time of 0 s (1), 30 s (2), 1 min (3), 3 min (4), 5 min (5) and 10 min (6) and electrochemical polymerization of PPy at 0.8 V versus Ag/AgCl for 600 s. Current density: 1 A $g^{-1}$.

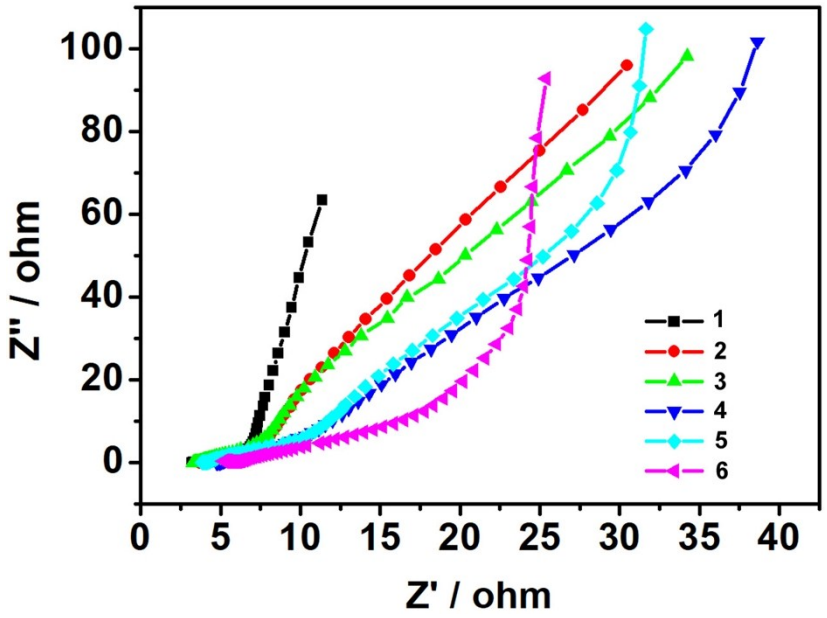


**Fig. S6** Electrochemical impedance spectroscopy of different Cu-TCPP/PPy electrodes through the electrophoretic deposition of wrinkled 2D ultrathin Cu-TCPP nanosheets for a certain time of 0 s (1), 30 s (2), 1 min (3), 3 min (4), 5 min (5) and 10 min (6) and electrochemical polymerization of PPy at 0.8 V versus Ag/AgCl for 600 s. Frequency range: 0.01 Hz~10 kHz. Electrolyte: 0.5 M $H_2SO_4$.

The electrochemical impedance spectroscopy of the pristine PPy and Cu-TCPP/PPy films with different contents of Cu-TCPP and PPy are measured to study the charge transfer resistance ($R_{ct}$) and ion transport. Nyquist plots of all Cu-TCPP/PPy electrodes show negligible semicircles and a quite low $R_{ct}$, reflecting a good ionic conductivity of the electrodes.[1] While, with the contents of Cu-TCPP nanosheets increasing, the $R_{ct}$ gradually becomes larger, suggesting that the hybrid of Cu-TCPP nanosheets has a significant effect on the electrocic conductivity of the PPy film. At high frequencies, the slope of the plot for the PPy-containing film shows a slightly higher diffusion resistance compared to pristine PPy film, presumably due to the presence of Cu-TCPP nanosheets. A sudden increase in the slope of sample 6 is ascribed to the absence of Cu-TCPP nanosheets in local areas.

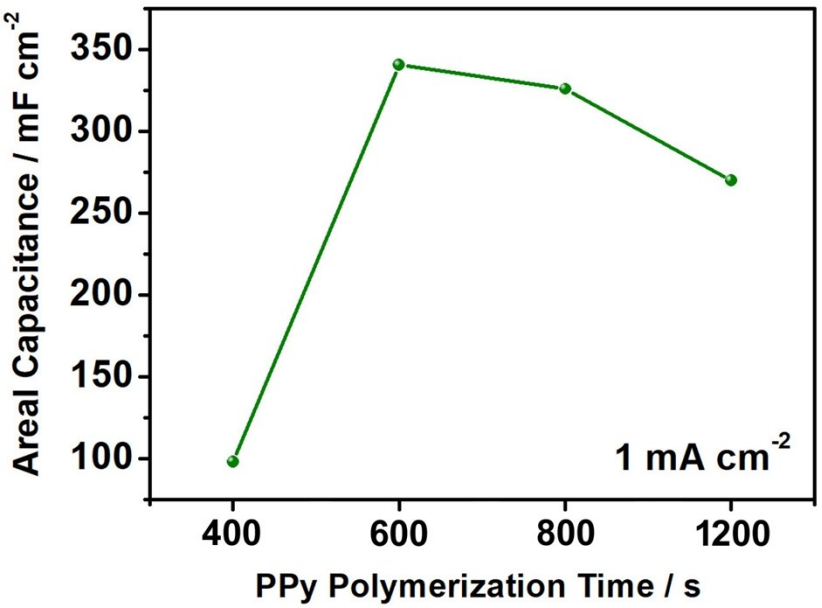


**Fig. S7** Areal capacitance of different Cu-TCPP/PPy electrodes through the electrophoretic deposition of wrinkled ultrathin 2D Cu-TCPP nanosheets for 30 s and electrochemical polymerization of PPy at 0.8 V versus Ag/AgCl for a certain time of 400 s, 600 s, 900 s and 1200 s. Current density: 1 mA $cm^{-2}$.

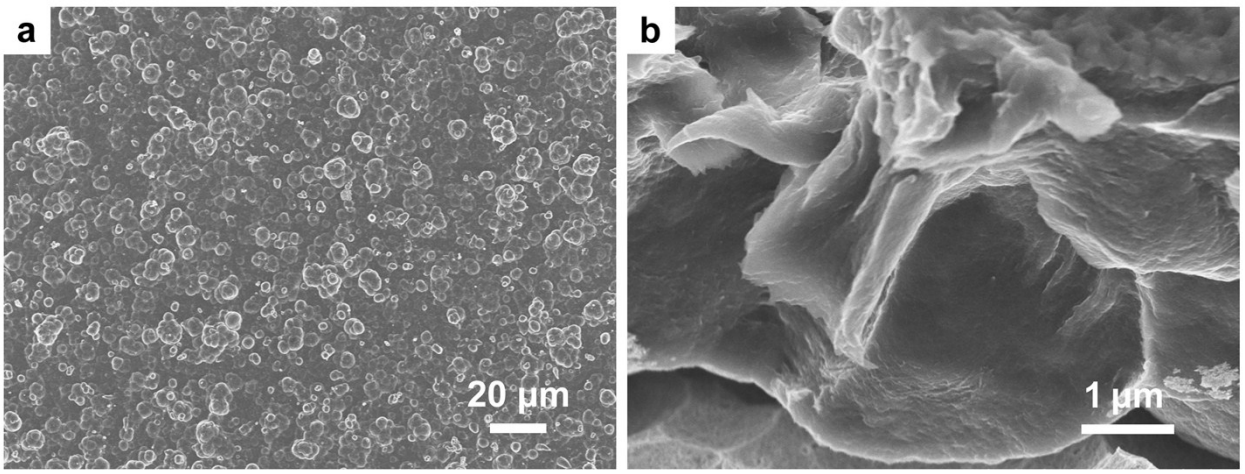


**Fig. S8** (a) The top-view SEM image and (b) cross-sectional SEM image of the Cu-TCPP/PPy film after cycling test.

**Table S1** Parameters of Cu-TCPP/PPy films through the flexible Cu-TCPP/PPy hybrid films through the combination of electrophoretic deposition method and electrochemical polymerization technology.

| Cu-TCPP/PPy film[a] | Mass | Size | Thickness |
|---|---|---|---|
| Cu-TCPP 0s | 1.7 mg | 1.0*1.4 $cm^2$ | 30 μm |
| Cu-TCPP 30 s | 1.8 mg | 1.0*1.4 $cm^2$ | 30 μm |
| Cu-TCPP 1 min | 1.8 mg | 1.0*1.4 $cm^2$ | 28 μm |
| Cu-TCPP 3 min | 1.8 mg | 1.0*1.4 $cm^2$ | 21 μm |
| Cu-TCPP 5 min | 1.8 mg | 1.0*1.4 $cm^2$ | 19 μm |
| Cu-TCPP 10 min | 1.8 mg | 1.0*1.4 $cm^2$ | 17 μm |

[a] The electrophoresis deposition time is set as 30 s, 1 min, 3 min, 5 min and 10 min. The PPy is electrochemical polymerized onto the wrinkled Cu-TCPP film under constant voltage of 0.8 V versus Ag/AgCl for 600 s.

1. M. Boota, B. Anasori, C. Voigt, M.-Q. Zhao, M. W. Barsoum and Y. Gogotsi, *Adv. Mater.*, 2016, **28**, 1517-1522.