SUPPLEMENTARY INFORMATION

Structure–Performance Relationship in Copper Phthalocyanine-Based Supercapacitor Electrodes: Influence of Substituent Geometry from Molecular Design to Electrochemical Function

Şirin Siyahjani-Gültekin[a]*, Berivan Arin Öztürmen[b], Damla Şahin[a], Gülşah Yilmaz[a], Bahar Tosun Ercan[a], Burak Gültekin[a], Zekeriya Biyiklioglu[b]*

[a]*Ege University, Solar Energy Institute, Bornova, Bornova, 35100, İzmir, Türkiye*
[b]*Karadeniz Technical University, Faculty of Science, Department of Chemistry, Trabzon, Türkiye*

1.1. Materials and Equipments

4-[(3,4,5-Trimethoxybenzyl)oxy]phthalonitrile (**TMe-CN**) was synthesized according to literature [1]. A DLAB RE100-pro Rotary device was used as the evaporator. Using the ATR method, the IR spectra were captured on a Perkin Elmer 1600 FT-IR Spectrophotometer. Microflex LT MALDI-TOF mass spectrometer Bremen, Germany. The UV–Vis absorption spectra were recorded on DLAB SP-XUV5101 UV-Vis spectrophotometer at room temperature. The used materials and types of equipment are presented as Supplementary Information. Carbon Black (CB, 99.9% surface area, 75 m^2/g) was obtained from Alfa Aesar. Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) with an average molecular weight of about 400,000 g/mol was obtained from Sigma-Aldrich and used as a binder on the electrode. The 250 μm in thickness flexible graphite sheets used as current collectors were obtained from Nickunj Eximp Enterprises.

Table S1. Comparison of the electrochemical performance of CuPc/phthalocyanine-based supercapacitor electrode

Material name / active type / structure type	Total mass in electrode & electrode area	Electrolyte	3-electrode or 2-electrode	Potential window	Current density / scan rate	Specific capacitance (as reported)	Energy density	Power density	Cycling stability	Reference	Difference from the present work
BTCuPc; Cu phthalocyanine; HMPM-bridged ball-type Cu phthalocyanine on GCE	GCE area 0.076 cm^2; areal loading 0.5 mg cm^{-2}	3.0 M KCl (aq.)	Three-electrode	1.5 V (−0.5 to 1.0 V vs Ag/AgCl)	2 A g^{-1}; 5 mV s^{-1}; 100 mV s^{-1}	265 F g^{-1} at 2 A g^{-1}; 264.8/265 F g^{-1} at 5 mV s^{-1}; 143.3 F g^{-1} at 100 mV s^{-1}	NR	NR	87.75% after 2000 CV cycles at 100 mV s^{-1}	[2]	Ball-type bridged CuPc on GCE; no matched peripheral/non-peripheral isomer comparison under identical substituent chemistry
$Co(NO_2)_4$Pc-rGO (1/6); Co phthalocyanine/rGO nanocomposite; tetranitro-substituted CoPc immobilized on rGO	NR	NR	Three-electrode	NR	4 A g^{-1}; 10–200 mV s^{-1} explored	150.22 F g^{-1} at 4 A g^{-1}	NR	NR	>100% after 5000 cycles at 10 A g^{-1}	[3]	Composite strategy dominated by rGO synergy; not a clean positional-isomer CuPc comparison
CuPc nanowires; pure Cu phthalocyanine; solution-processed nanowire film on Ni foam	10 mg active material on 2 × 1 cm^2 Ni foam	1.0 M NaOH	Three-electrode	0–0.6 V vs Ag/AgCl (CV); 0–0.5 V vs Ag/AgCl (GCD)	5–100 mV s^{-1}; 0.3 A g^{-1}	406 F g^{-1} at 5 mV s^{-1}; 260 F g^{-1} at 0.3 A g^{-1}	NR	NR	~85% retention after 3000 GCD cycles at 6 A g^{-1}	[4]	Pure CuPc morphology-controlled nanowire system; no substituent-position effect and no matched isomer pair
NiF/rGO2-2; MnPc/rGO hybrid; non-peripheral carbazole-substituted MnPc electrodeposited with rGO on Ni foam	Ni foam substrate; active mass defined on NiF, exact loading not clearly visible in extracted text	2.0 M KOH	Three-electrode for electrode tests; ASC also assembled	0–0.5 V (electrode); 0–1.5 V (ASC)	0.5–10 A g^{-1}; 10–50 mV s^{-1}	512.4 F g^{-1} at 0.5 A g^{-1}	17.4 Wh kg^{-1} (ASC)	375 W kg^{-1} (ASC)	88.1% after 5000 cycles at 10 A g^{-1} (electrode); 74.6% after 5000 cycles at 5 A g^{-1} (ASC)	[5]	Also studies peripheral/non-peripheral substitution, but in a MnPc/rGO hybrid and partly device-level ASC format
$NiMe_2$Pc/CNT-COOH (6:10); Ni phthalocyanine/CNT nanocomposite; peripheral octamethyl-	1 mg active material per electrode on carbon paper/carbon	1 M H_2SO_4 (three-electrode); PVA/H_2SO_4 gel for	Three-electrode for electrode tests; two-electrode	Device: 1.0 V for single SC; 3.0 V for three	0.25 A g^{-1} (best electrode/device Cs); 100 mV s^{-1} used in CV comparisons	330.5 F g^{-1} at 0.25 A g^{-1} (electrode); 164.4 F g^{-1} at 0.25 A g^{-1}	22.8 Wh kg^{-1} (solid-state	2469.6 W kg^{-1} (solid-state SC); 250 W	111.6% after 35,000 cycles at 8 A g^{-1} (solid-state SC);	[6]	Peripheral NiPc/CNT composite optimized for practical solid-

substituted NiPc on carboxylated CNT dendritic network	cloth (2 cm × 1 cm × 0.1 cm)	solid-state device	symmetric all-solid-state SC/FSC devices also assembled	devices in series		(solid-state symmetric SC)	SC); 52.1 Wh kg^{-1}	kg^{-1} (FSC)	95.4% after 35,000 cycles for FSC		state/flexible devices; unlike the present work, performance depends strongly on CNT conductive matrix and device engineering
$Ni_2[CuPc(NH)_8]$/EG-2; phthalocyanine-based 2D c-MOF/graphene hybrid; exfoliated nanosheet MSC electrode	Total active mass NR; interdigital in-plane pattern with 8 fingers (width 1 mm, length 10 mm, interspace 1 mm) on PI substrate	PVA/LiCl gel electrolyte	In-plane all-solid-state MSC device	NR	2–50 mV s^{-1}; 0.04–0.4 mA cm^{-2}	18.9 mF cm^{-2} at 0.04 mA cm^{-2}	NR	NR	Outstanding cycling stability reported, but explicit retention value/cycle number not clearly visible in extracted main text	[7]	Fundamentally different architecture: 2D c-MOF nanosheet/graphene micro-supercapacitor with areal capacitance metrics rather than conventional powder-film CuPc electrode comparison
n-TMe-Cu (this work); CuPc derivative; non-peripheral tetra-(3,4,5-trimethoxybenzyl)oxy-substituted CuPc, CB/PVDF-HFP film on flexible graphite	1 mg active material on 1 cm^2	1 M H_2SO_4	Three-electrode	NR	1 A g^{-1} (0.2–2.0 A g^{-1} explored)	360 F g^{-1} at 1 A g^{-1}	67 Wh kg^{-1}	99.97 W kg^{-1} at 0.2 A g^{-1}	80% after 5000 cycles at 2 A g^{-1}	This work	-

References

[1] M. S. Ağırtas, B. Cabir, S. Özdemir, Novel metal (II) phthalocyanines with 3,4,5-trimethoxybenzyloxy-substituents: Synthesis, characterization, aggregation behaviour and antioxidant activity, Dyes and Pigments 96 (2013) 152-157. https://doi.org/10.1016/j.dyepig.2012.07.023.

[2] N. Koçyiğit, M. B. Arvas, S. Yazar, N. Açar-Selçuki, Y. Şahin, M. Özer and Ö. Bekaroğlu, Synth. Met., 2023, 292, 117242. https://doi.org/10.1016/j.synthmet.2022.117242

[3] F. Qi, Y. Wang, J. Xu, X. Wang, J. Wang, H. Shan, M. Li and J. Xu, Synth. Met., 2023, 293, 117284. https://doi.org/10.1016/j.synthmet.2023.117284

[4] M. Samanta, P. Howli, U. K. Ghorai, M. Mukherjee, C. Bose and K. K. Chattopadhyay, Phys. E Low-Dimens. Syst. Nanostruct., 2019, 114, 113654. https://doi.org/10.1016/j.physe.2019.113654

[5] H. Y. Yenilmez, N. Farajzadeh Öztürk, Ö. Budak, Ö. İpsiz Öney, A. Koca and Z. Altuntaş Bayır, Chem. Asian J., 2024, 19, e202400938. https://doi.org/10.1002/asia.202400938

[6] Y. Wang, M. Li, R. Ramachandran, H. Shan, Q. Chen, A. Luo, F. Wang and Z.-X. Xu, J. Energy Chem., 2023, 76, 214–225. https://doi.org/10.1016/j.jechem.2022.08.046

[7] M. Wang, H. Shi, P. Zhang, Z. Liao, M. Wang, H. Zhong, F. Schwotzer, A. S. Nia, E. Zschech, S. Zhou, S. Kaskel, R. Dong and X. Feng, Adv. Funct. Mater., 2020, 30, 2002664. https://doi.org/10.1002/adfm.202002664