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Boosting the Capacitive Performance of Cobalt(II) Phthalocyanine by Non-peripheral Octamethyl Substitution for Supercapacitors[†]

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Main observation and conclusion

In this paper, pristine cobalt(II) phthalocyanine (CoPc) and non-peripheral octamethyl substituted CoPc (N-CoMe₂Pc) are the focus of electrochemical investigation. CoPc and N-CoMe₂Pc nanorods (NR) were synthesized by a facile precipitation process from sublimated bulk phthalocyanine powders and their electrochemical properties were explored. Due to the large specific surface area, the capacitance performance of the nanorods was significantly higher than that of the sublimated powder sample. N-CoMe₂Pc powder exhibited better pseudocapacity compared with CoPc powder and CoPc NR, which is attributed to enhanced charge transfer rate and improved redox activity after the introduction of octamethyl substituents on phthalocyanine ring. The maximum specific capacitance value was achieved by N-CoMe₂Pc NR based electrode, exhibiting 210.2 F g⁻¹ capacitance at 5 mV s⁻¹ scan rate and 156.1 F g⁻¹ at 0.25 A g⁻¹ current density, and also showing high efficiency and satisfactory retention. These results indicate that according to proper molecular design, N-CoMe₂Pc NR could be applied as the potential candidate for electrode material in supercapacitors.

Comprehensive Graphic Content



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[†] Dedicated to Department of Chemistry, SUSTech, on the Occasion of her 10th Anniversary.

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Background and Originality Content

In order to cope with the shortage of fossil energy, the proportion of clean energy will significantly increase in the next decade.^[1] But the production processes of the new energy sources are unstable, such as wind and solar energy, so energy storage devices are required to store the energy first. And coupled with the rapid development of flexible wearable electronic devices, a high-performance and light-weight device for energy storage has aroused considerable interest of researchers.^[2-3] Supercapacitors, which are also called electrochemical capacitors, can stand out among various energy storage devices due to their ideal features like outstanding power density, fast charging and discharging rates, long cycle life, low maintenance costs, etc.^[4] Generally, supercapacitors are divided into two types according to their main charge storage mechanism, namely, electric double layer capacitors (EDLC), which release and store energy at the interface of electrode/electrolyte by electrostatic interaction, and pseudocapacitors through the faradic redox reaction of electrode materials.^[5] It is reported that carbon-based materials have been widely used in EDLC, which can provide better electrochemical activity but suffer from weaknesses such as narrow operating voltage windows and lower capacitance value.^[6] Alternatively, pseudocapacitor materials, like transition metal oxides and conductive polymers, are able to provide higher specific capacitance than EDLC, which received more attention from researchers.^[7-8]

Metal phthalocyanine is a kind of macrocyclic compounds with 18 π -conjugated electron aromatic cloud delocalized around the macrocycle. In general, the metal phthalocyanines are found as a Pc^{2-} , which tightly adsorbs lots of ions in the oxidation state of +2, such as Cu^{2+} , Co^{2+} and $Fe^{2+[9]}$ It is extremely hard or even impossible to extract metal ions from the central cavity of metal phthalocyanines, unless the entire macrocyclic structure is destroyed.^[10] However, the central metal ion can undergo redox reaction, and the pyrrole N in phthalocyanine ring is prone to proton reaction, resulting in highly electrochemical reversibility and the ultrafast redox reactions.^[11-12] The phthalocyanine ring interacting with the metallic ion can provide excellent charge transport capacity, which can lead to excellent electrochemical performance.^[13] As a consequence of their electrochemical activity, metal phthalocyanines have been used in plenty of electrochemical fields such as electrocatalysis,^[14] electrochemical sensors,^[15] and batteries.^[16] However, the application of metal phthalocyanines as supercapacitor electrodes is less explored. In 2010, Ozoemena et al. have evaluated the supercapacitive behavior of nickel(II) octa [(3,5-biscarboxylate)-phenoxy] phthalocyanine (NiOBCPPc), exhibiting ~54 mF cm⁻² geometrical capacitance at a current density of 138 μ A cm⁻².^[17] Mu *et al.* have fabricated a three-dimensional flower-like nanostructure of iron tetranitrophthalocyanine (TNFePc) for supercapacitors and a specific capacitance value of 63 F g^{-1} at 0.3 A g^{-1} was obtained. $^{[18]}$ Koodlur et al. have synthesized palladium tetra aminephthalocyanine (TNPdPc) coating on glassy carbon electrode, showing 146 F g^{-1} capacitance at a scan rate of 5 mV $s^{-1}\,^{[19]}$ NiPc nanofibers were prepared by Madhuri and his coworkers using an ultrasound method, the calculated capacitance value was 52.28 F g^{-1} (1 A g^{-1}) in 1 M H₂SO₄ solution.^[20] Recently, Xu et al. have fabricated the non-peripheral octamethyl substituted copper(II) phthalocyanine (N-CuMe₂Pc) nanorods via precipitation for supercapacitor electrode material performing in 1 M H₂SO₄ electrolyte, the obtained capacitance value was 84.3 F g^{-1} at a current density of 0.5 A g^{-1} . After that, they built a composite of N-CuMe₂Pc nanorods and Mxene nanosheets, the performance of the capacitor was further improved.^[13] In our previous works, various peripheral and non-peripheral methyl substituted metal phthalocyanines have been used in organic field-effect transistor,^[21] perovskite solar cell,^[22] organic memristor^[23] as well as supercapacitor.^[13] Though few works reported phthalocyanine based materials for supercapacitors, the basic substitution of phthalocyanine may vary the electrochemical performance. The size effect and the substituents influence of phthalocyanine for supercapacitor application are still unclear and need to be figured out.

In this work, we compared the supercapacitor performance of pristine cobalt(II) phthalocyanine (CoPc) and non-peripheral octamethyl substituted cobalt(II) phthalocyanine (N-CoMe₂Pc) based on their sublimated powder form and nanostructure. As far as we can acknowledge, this is the first time to investigate the influence of methyl substituents on the pseudocapacity of phthalocyanines from the perspective of molecular structure design. The experimental results show that the pseudocapacitance activity of N-CoMe₂Pc molecules is enhanced due to hyper-conjugation effect of methyl groups, and the conductivity of the material is also enhanced because of the increased intermolecular force. In addition, the presence of methyl groups obstructs the one-dimensional aggregation of phthalocyanine molecules in the preparation process of nanostructures, which facilitates the exposure of more active sites in the electrode material, and will directly promote rapid ion transport at the electrode/electrolyte interface. Therefore, the capacitance performance of N-CoMe₂Pc NR is improved comparing with other three materials, suggesting that it is a good candidate for pseudo capacitor materials.

Results and Discussion

Structural analyses

The general synthesis procedure of CoPc and N-CoMe₂Pc are outlined in Supporting Information (Scheme S1), which involve a one-step synthesis from phthalonitrile and 3,6-dimethyl phthalonitrile. The detailed synthetic information of Pc samples and Pc nanostructure was described in the experimental section. The as fabricated CoP and N-CoMe₂Pc samples after sublimation were denoted as CoP and N-CoMe₂Pc, respectively. And the CoP and N-CoMe₂Pc nanorod samples were denoted as CoP NR and N-CoMe₂Pc NR, respectively.

The optical properties of as-sublimated phthalocyanines and corresponding nanostructures were investigated by UV-vis absorption spectrometer. Figure 1a presents the UV-vis spectra with monomeric absorption of as-sublimated powders dissolved in 1-chloronaphthalene. Both samples of CoPc and N-CoMe₂Pc exhibit two strong absorbance bands: the Q band located at 600-750 nm which is assigned to the $a_{1u}(\pi)$ - $e_g(\pi^*)$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) in the phthalocyanine ring structure, and the Soret band (B band) at 300-400 nm derived from the deeper $a_{2u}(\pi)$ to LUMO transition. $^{[24]}$ The Q-band main peak of N-CoMe₂Pc shows 23 nm redshifts compared with that of CoPc due to stronger π -conjugation interaction, which is beneficial for the charge transport ability of the material. Figure 1b presents the UV-vis spectra of as-precipitated nanorods dispersed in dichloromethane (DCM). The nanorod formed by self-assembly in solution is an aggregated form of phthalocyanine molecules. The absorption bands of both nanorods in the visible region have a triple-peak structure because of Davydov splitting, which is attributed to the interaction between transition dipole moments of the adjacent phthalocyanine molecules with different orientations that are close enough to emerge electronic transitions.^[25] The broad absorption Q-band of N-CoMe₂Pc NR is divided into three peaks at 626.7, 690.0 and 761.7 nm, giving a red shift (615.1, 662.6 and 757.8 nm, respectively) relative to that of the CoPc NR. The intensity of the higher energy peak of CoPc NR is weaker than the lower energy peak compared with that of

670 nn 693 nm 1.0 (b) (a) CoMe Po a.u. Absorbance 0. 0.4 0.3 0.0 600 700 800 500 800 400 500 900 300 400 600 700 Wavelength / nm Wavelength / nm 150 (d) (c) 375 000 CoPc N-CoMe,Pc -6 120 CoPc NR N-CoMe,Pc NR Quantity absorbed / (cm Absorption / a.u. 90 60 3 2500 2000 1500 500 0.2 0.4 0.6 3000 1000 0.0 0.8 1.0 Wa Relative **J**

Figure 1 (a) UV-vis absorption spectra of CoPc, N-CoMe₂Pc in 1-chloronaphthalene; (b) UV-vis absorption spectra of CoPc NR, N-CoMe₂Pc NR in DCM; (c) FTIR spectra of as-sublimated CoPc, N-CoMe₂Pc powder; (d) BET isotherms of phthalocyanine powders and nanostructures.

N-CoMe₂Pc NR, which confirms the β -phase of CoPc.^[25,26]

The FTIR spectra of the synthesized CoPc and N-CoMe₂Pc powders are presented in Figure 1c. The peaks of both two phthalocyanines observed in range from 500 to 1600 cm⁻¹ originate from the vibrations in phthalocyanine skeleton structures. In the FTIR spectrum of CoPc, the peaks at 724, 1288, 1336, 1428 and 1535 cm⁻¹ are coming from the phthalocyanine ring vibrations. The peaks appeared at 1151 and 1612 cm⁻¹ are assigned to the C-H bending vibrations of the aromatic ring and C=N-C stretching. The band at 916 cm⁻¹ is relevant to Co-N band, indicating the coordinated interaction between the 3d unoccupied orbital of Co and N in the phthalocyanine ring. The characteristic weak peaks at 3050 cm^{-1} are attributed to the C–H stretching in aromatic rings.^[27] In the FTIR spectrum of N-CoMe₂Pc, the above peaks are all present but with some shifts caused by the introduction of octamethyl groups. Meanwhile, some characteristic peaks of methyl groups are emerging. The peaks exhibiting between 2800 and 3000 cm^{-1} are signed to C—H stretching in alkanes. The bands at 1375 and 1242 cm^{-1} are rooting in C—H bending and wagging in alkanes, respectively,^[21] which also confirms the formation of N-CoMe₂Pc.

The morphologies of as-sublimated phthalocyanines were investigated by SEM. As shown in Figures 2a and 2b, the as-sublimated CoPc and N-CoMe₂Pc powders demonstrate big micronsized rods like structure due to very strong aggregation between phthalocyanine molecules during the sublimation process used for purification of the crude products. CoPc presents a needle-like shape with a length of more than 100 microns, and the length is significantly reduced to around 10 microns after the introduction of methyl groups, indicating that the methyl group can inhibit the one-dimensional aggregation of phthalocyanine molecules during sublimation. The morphologies of as-fabricated phthalocyanine nanostructures were investigated by TEM. The images in Figures 2c and 2d show that CoPc nanostructure contains nanorods (length < 1 μ m, width < 100 nm), and the N-CoMe₂Pc nanostructure is also mainly composed of nanorods (length < 300 nm, width < 30 nm) which are smaller than those of the CoPc NR, further confirming the presence of methyl group can also prevents the one-dimensional aggregation of phthalocyanine molecules during the self-assembly process in DI water. For supercapacitor electrode material, small size often means larger specific surface area,



Figure 2 SEM images of (a) as-sublimated CoPc and (b) N-CoMe₂Pc powders; TEM images of (c) as-precipitated CoPc NR and (d) N-CoMe₂Pc NR; HRTEM images of (e) as-precipitated CoPc NR and (f) N-CoMe₂Pc NR.

more reactive sites, and shorter charge transfer distance, which is anticipant to elevate the performance of supercapacitor.^[28] Clear and successive lattice fringes of CoPc NR and N-CoMe₂Pc NR can be observed in the HRTEM images (Figures 2e and 2f), indicating the high crystallinity of phthalocyanines nanostructure fabricated by solution precipitation process.

The BET surface areas of the four materials were investigated by N₂ adsorption-desorption at 77.1 K. As shown in Figure 1d, all of the isotherms present classic type IV profiles with H3 hysteresis loops at relative pressures between 0.5 and 1.0 p/p_0 , indicating the presence of mesopores in materials.^[29] Various surface areas of 37.63, 25.45, 18.09 and 13.43 $\textrm{m}^2~\textrm{g}^{-1}$ were obtained by N-CoMe₂Pc NR, CoPc NR, N-CoMe₂Pc and CoPc, respectively. BET surface areas of phthalocyanine nanostructures are higher than those of the powders, which is attributed to the size reduction of phthalocyanine with nanostructure. Since the real pores were not discerned in the phthalocyanine rods, it is assumed that the mesoporous behavior may come from the voids among the rods.^[30] It is known that high surface area could be favorable for more active sites exposure in electrode material and directly promote the rapid migration of ions at the electrode/electrolyte interfaces, which can increase the utilization of the electrode material and leads to a larger specific capacitance value; and nanosized material can shorten the charge transfer distance, thereby reducing resistance.^[31] Therefore, the larger surface area of N-CoMe₂Pc NR is likely to elevate its electrochemical performance for supercapacitor electrode.

Figure 3 shows XRD patterns of as-sublimated powder and nanorods samples for both phthalocyanines. The XRD patterns of both as-sublimated CoPc and N-CoMe₂Pc powders demonstrate sharp peak at 2θ value of around 7°, which is the characteristic peaks of a metal phthalocyanine.^[32] It is worth to note that comparing with CoPc, both N-CoMe₂Pc samples exhibit a high intensity peak at 26.30° (2θ) (inter-planar spacing: 3.387 Å) inducing from face-to-face stacking of phthalocyanine rings.^[22] This result indicates that introduction of the octamethyl groups gives rise to stronger intermolecular π - π stacking interactions between N-CoMe₂Pc molecules, which is consistent with the conclusion observed through UV-vis spectra. The XRD pattern of CoPc NR shows sharp peaks and keeps almost same with CoPc powder. The appearance of diffraction peaks at around 20 value of 7.12° and 26.30° in the XRD pattern of the N-CoMe₂Pc NR suggests that the structure of phthalocyanine has not changed. These two peaks become broader caused by large atomic relaxation appearing on nanoscale material surfaces. Comparison of XRD peaks of N-CoMe₂Pc powder and N-CoMe₂Pc NR indicates an obvious increasement of molecular arrangement ordering in self-assembled nanorods. Through a comparison of self-assembly behaviors of CoPc NR and N-CoMe₂Pc NR, it reveals that the strong π - π interaction can be maintained after precipitation process because of the



Figure 3 XRD patterns of phthalocyanine as-sublimated powders and nanorods.

methylation, which can improve the self-assembly capability and is beneficial to the charge transport in subsequent application. $^{\left[23\right]}$

The elemental composition and surface electron state of CoPc and N-CoMe₂Pc were studied by XPS. The survey spectra in Figures 4a and 4b show that C, N and Co are present in both CoPc and N-CoMe₂Pc. The element of oxygen is most likely to come from oxygen-containing pollutants adsorbed on the surface of the samples. Figure 4c shows the N 1s high resolution XPS spectrum of CoPc, which is able to deconvoluted into peaks at 399.32 and 401.30 eV that can be identified as C-N=C and N-Co bonds, respectively. The N 1s high resolution XPS spectrum of N-CoMe₂Pc shows two peaks at 399.12 and 401.08 eV (Figure 4d), and the binding energy of these peaks has a negative shift after the introduction of octamethyl groups, which may result from that the hyper-conjugation effect of the methyl groups would increase the electron cloud density on the phthalocyanine ring.^[33,34] The lower binding energy is assigned to higher electron cloud density around the bond, which also presents enhanced electrochemical activity and more violent protonation reaction, which is expected to increase the capacitance. The Co 2p high resolution XPS spectrum of CoPc (Figure 4e) suggests that the two peaks located at 781.40 and 796.68 eV corresponds to Co $2p_{3/2}$ and Co $2p_{1/2}$, respectively. The splitting between these two peaks is 15.3 eV, indicating that cobalt species is in the formal Co^{2+} valence state.^[35] The curve of Co 2p XPS spectrum of N-CoMe₂Pc (Figure 4f) can be fitted by two main peaks at 781.22 and 796.56 eV that are also showing slight shift due to the fluctuation of electron cloud density in the phthalocyanine ring.

Electrochemical characterization

The electrochemical responses of powders and nanorods of CoPc and N-CoMe₂Pc were assessed as electroactive materials for supercapacitor electrodes, in terms of cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) in 1 M H_2SO_4 solution applying a three-electrode configuration.



Figure 4 XPS spectra of the (a) survey, (c) N 1s and (e) Co 2p regions for CoPc powder; (b) survey, (d) N 1s and (f) Co 2p regions for N-CoMe₂Pc powder.

Figures 5a—5d exhibit the CV curves of four different cobalt(II) phthalocyanines at scan rate 5-100 mV s⁻¹. First of all, the "Capacitive Potential Range (CPR)" of electrodes is optimized in between 0 to 1 V. After increased the upper and lower potential range, it is noticed the current level increased with a sharp hump, resulting from hydrogen and oxygen evolution reactions. Thus, the voltage window was selected from 0 to 1.0 V according to the CV test. The CV curve shape of these electrodes is distinctive with that of carbon materials, which generally give a rectangular-like curve denoting EDLC. Meanwhile, all of these CV curves present some strong peaks, which implies that the capacitance of these electrodes mainly comes from pseudocapacitive capacitance based on a redox mechanism.^[36] The CV curves of CoPc powder (Figure 5a) reveals a redox couple at around 0.85 and 0.65 V corresponding to the faradic redox-reactions of Co(II)/Co(III), which is consistent with other cobalt phthalocyanines that have been reported.^[37,38] Additionally, nickel phthalocyanine and copper phthalocyanine have also been reported to undergo a similar redox process of central metal in supercapacitor application.[12,39] Another redox couple peaks appear at around 0.4 and 0.55 V, corresponding to the redox-reactions of the pyrrole like nitrogen groups in CoPc, which is also known as the protonation and deprotonation of phthalocyanine molecules.^[20] This process is more pronounced in acidic media and can greatly improve the charge mobility of electrode material and elevate the electron transfer rate during electro-catalytic reactions.^[40] Figure 5b shows the redox peaks current of N-CoMe₂Pc powder are getting higher compared with CoPc powder, and the peak positions are also deviated. The specific capacitance is calculated to be 94.2 F g^{-1} at a scan rate of 5 mV s⁻¹, which is about 4.6 times higher than that of CoPc (20.4 F g^{-1}). It is probably ascribed to three reasons: (1) The size of N-CoMe₂Pc powder after sublimation is smaller, which is conducive to the reaction between more active sites of the electrode material and electrolyte ions; (2) The introduction of methyl groups improves the electrochemical activity of electrode material due to the increased electron cloud density in molecules; (3) The introduction of methyl groups enhances the intermolecular accumulation and reduces the charge transfer resistance inside the material.

With the scan rates increasing from 5 to 100 mV s⁻¹, the redox peak current increases correspondingly, and the potential of the oxidation peak and the reduction peak shift in the positive and



Figure 5 Cyclic voltammetry response of (a) CoPc powder; (b) N-CoMe₂Pc powder; (c) CoPc NR; (d) N-CoMe₂Pc NR; and (e) the four electrodes at 20 mV s⁻¹ scan rate (f) Specific capacitance of the four electrodes at different scan rates.

negative directions, respectively, indicating a rapidly reversible faradic reaction occurs between the electroactive electrode material and the electrolyte ions and the shift is attributed to the polarization of electrode material beside the rapid electronic/ionic interactions at high scan rate.^[7] It is noted that the specific capacitance is inversely proportional to the scan rate. This is mainly caused by the faster reaction of the electrode at high scan rate, and the diffusion rate of the electrolyte from the electrode/electrolyte interfaces into the electrode material is insufficient to meet the redox reactions.^[41] Meanwhile, this rapid reaction in electrodes cause the weakening of the oxidation peak, which is more obvious at lower scan rate. As the evidence of Figure 4f, the specific capacitance values of the four electrodes are reduced by at least half at higher scan rate. Conversely, the electrolyte ions can efficiently disseminate into the electrode materials at lower scan rate, which results in adequate redox reactions at the solid/liquid interfaces and provides higher specific capacitance values.^[40]

Figures 5c and 5d show the CV curves of CoPc NR and N-CoMe₂Pc NR at various scan rates, respectively. It is observed that the positions of the redox peaks remain unchanged compared with their powders, but the intensity of all peaks increase significantly, which corresponds to the improvement in capacitance. This is attributed to the increasement of specific surface area of the phthalocyanine nanocrystals.^[42] It is worth noting that although the size of CoPc nanocrystals is much smaller than that of sublimated N-CoMe₂Pc powder, its capacitance performance is still weaker than the latter, indicating the introduction of methyl groups on the phthalocyanine ring is more critical to the im-

provement of the capacitance performance of electrode material. As expected, it is shown from Figure 5d that the area enclosed by the CV curve of N-CoMe₂Pc NR is further enlarged, and the specific capacitance value reaches 210.2 F g⁻¹ at lower scan rate (5 mV s⁻¹), and it remains 93.8 F g⁻¹ at higher scan rate (100 mV s⁻¹), demonstrating good capacitance performance, which indicates that N-CoMe₂Pc has great potential for supercapacitor electrode. Figure 5e shows the comparison of the CV curves of four electrode materials at same scan rate. It can be seen intuitively that their capacitance performance is ranked as follows: N-CoMe₂Pc NR > N-CoMe₂Pc > CoPc NR > CoPc.

Figures 6a—6d present the galvanostatic discharging curves of bulk and nanostructured phthalocyanines within a potential window from 0.1 to 1.0 V at various current densities. The discharge curves of four phthalocyanine samples are non-linear and show two plateaus originating from the pseudocapacitance behavior on electrodes, which keeps in line with the CV results.^[42] The specific capacitance calculation formula given in the experimental part demonstrates that the longer discharge time corresponds to the better the capacitance performance of the material. It can be seen from Figures 6a-6d that the specific capacitance is a monotonically decreasing function of current density, which is similar to the CV results. This is because only part of the charging and discharging process can be performed on the electrode surface under high current density, which reduces the utilization rate of the active material, resulting in a decrease in the specific capacitance obtained.[43]

It is clearly shown in Figure 6e that the discharge time of octamethyl substituted cobalt(II) phthalocyanines are significantly longer than that of pristine cobalt(II) phthalocyanines no matter with powder form or nanostructure at the current density of 0.5 A g⁻¹, and the N-CoMe₂Pc NR exhibited a prolonged discharge time, which is due to the introduction of methyl groups and the reduction of material size. As shown in Figure 6f, a maximum specific capacitance of 156.1 F g⁻¹ is achieved by N-CoMe₂Pc NR at a current density of 0.25 A g⁻¹ which is much higher than the N-CoMe₂Pc powder (80.6 F g⁻¹), CoPc NR (29.8 F g⁻¹) and CoPc powder (11.1 F g⁻¹), respectively. The specific capacitance of N-CoMe₂Pc NR electrode is 156.1, 136.2, 120.5, 107.3, 94.2, 90.6 F g⁻¹ at current densities of 0.25, 0.5, 1, 2, 4, and 5 A g⁻¹, respectively, showing a satisfactory rate capability.

The kinetics of the four electrodes was further investigated by EIS analysis. As shown in Figure 7a, all the Nyquist plots demonstrate a similar shape, which is constituted by a straight line at the lower frequency region and a semicircle at the higher frequency region. Figure 7b shows the enlarged spectra of Nyquist plots at the high-frequency region, the intercept on the real axis denotes the electrolyte resistance (R_s) , and the diameter of the semicircle refers to the charge transfer resistance of the electrode/electro-lyte interfaces (R_{ct}) .^[44] The electrodes of octamethyl substituted CoPc exhibited a smaller semicircle at the high-frequency region than pristine CoPc, suggesting the enhanced charge transfer rate while adding methyl groups, which is consistent with the previous conclusion. Similar result was obtained in previous research report. The addition of peripheral octamethyl groups on CuPc enhances the strength of molecular conjugate stacking and increases the carriers transfer rate of hole transport layer, resulting a higher photo-electric conversion efficiency of pervoskite solar cells.^[45]

All of the Nyquist curves have been fitted by the equivalent circuit (inset diagram of Figure 7a), and the simulated R_s and R_{ct} values of CoPc, CoPc NR, N-CoMe₂Pc, N-CoMe₂Pc NR can be determined as 1.249, 1.186, 1.126, 0.939 Ω and 2.836, 1.942, 1.857, 0.861 Ω , respectively. The lowest R_s and R_{ct} values of N-CoMe₂Pc NR proves the better ion diffusion pathways and charge transfer rate between the electrode/electrolyte interfaces. In addition, the straight line of Nyquist plot in the low-frequency region reveals the Warburg impedance (R_w), which represents ideal capacitive



Figure 6 Galvanostatic discharging curves at different current densities (a) CoPc powder; (b) N-CoMe₂Pc powder; (c) CoPc NR; (d) N-CoMe₂Pc NR; and (e) the four electrodes at 0.5 A g^{-1} current density (f) Specific capacitance of the four electrodes at various current densities.

characteristics.^[46] The straight line of the N-CoMe₂Pc NR is much closer to the imaginary axis, which demonstrated the better charge storage performance. The electrode of N-CoMe₂Pc NR with low contact resistance and charge transfer resistance is favorable for the rapid formation of reversible faraday reaction, thus improving the electrochemical performance. Furthermore, the phase angles change with the applied frequencies as shown in the bode plots (Figure 7c). It can be observed that the phase angles of the four prepared electrodes are close to 45°–65° when the frequency is less than 100 Hz, which involves the good pseudocapacitance behavior.^[47] The N-CoMe₂Pc NR electrode shows higher phase angles at the lower frequency, manifesting the faster charge transfer rate, which keeps in line with cyclic-voltammetry and discharging profiles.

Conclusions

In summary, we have investigated the pseudo capacitive behavior of CoPc NR, N-CoMe₂Pc NR, as-sublimated CoPc and N-CoMe₂Pc powder in acid medium. The capacitance performance of the nanorods were significantly higher than that of the as-sublimated powder sample due to the larger specific surface area after precipitation process. The as-sublimated N-CoMe₂Pc powder showed higher pseudocapacity compared with CoPc powder and nanorods, which is attributed to enhanced charge transfer rate and improved redox activity after methylation. Meanwhile, it reveals that the introduction of octamethyl substituents on the phthalocyanine ring is more critical to the improvement of the capacitance performance of phthalocyanines. The N-CoMe₂Pc NR showed maximum capacitance of 210.2 F g⁻¹



Figure 7 (a) Nyquist plots, inset: equivalent circuit diagram; (b) partial enlarged Nyquist plots and (c) Bode plots of phthalocyanine as-sublimated powders and nanorods.

at 5 mV s⁻¹ scan rate and 156.1 F g⁻¹ at 0.25 A g⁻¹ current density, and also showed high efficiency and satisfactory retention. So it can be used as a promising material for application in future supercapacitors. Furthermore, the specific capacitance will be improved by incorporating some EDLC materials, which helps to enhance the specific surface area and leads to synergistic effect.

Experimental

Synthesis of CoPc and N-CoMe₂Pc

For the synthesis of CoPc powder, phthalonitrile (2.50 g, 19.5 mmol), cobalt(II) chloride (0.633 g, 4.88 mmol), and quinoline (5 mL) was mixed in a 15 mL flask. It was stirred and heated at 170 °C surrounding by argon for 60 min, and then it was put in the air to cool down. Then the obtained mixture was washed by deionized water (DI water), ethanol, DCM and tetrahydrofuran (THF) successively in the filter paper to collect solid powder and dried at 80 °C. After that, the purity of phthalocyanine was further improved *via* vacuum sublimation (475 °C, ~5 × 10⁻⁴ Pa).

N-CoMe₂Pc powder was fabricated referring to previous literature.^[48] A mixture of 3,6-dimethylphthalonitrile (1.0 g, 5.12 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.2 mL), CoCl₂ (0.277g, 1.71 mmol) and 1-pentanol (5 mL) was put in a 15 mL flask. A dark green mixture was obtained by stirring at 140 °C under argon. The subsequent purification steps are consistent with the aforementioned.

Synthesis of N-CoMe₂Pc NR and CoPc NR

N-CoMe₂Pc NR and CoPc NR were prepared according to a

reported precipitation method with minor modification.^[23] Specifically, the phthalocyanine powder (20 mg) was dissolved into methanesulfonic acid (10 mL) and treated with ultrasonic waves for several minutes to reach a state of full dissolution. The solution (2.5 mL) was then added dropwise into the stirred DI water (200 mL) at a rate of 1-1.5 mL min⁻¹. The suspensions containing phthalocyanine nanostructures were centrifuged and the sediments were washed with DI water, ethanol, and acetone. Finally, the sediments on the filter paper were left to dry naturally at room temperature.

Electrochemical measurements

The electrodes of supercapacitor were prepared by following steps: Firstly, active material (as-sublimated phthalocyanine powders or as-precipitated phthalocyanine nanostructures) was mixed with carbon black as a weight ratio of 85:10 and then the mixed powder was dispersed in 5 weight % of Nafion and ethanol mixture. Then the resulting slurry was coated onto the carbon paper current collector (2 cm × 1 cm × 0.1 cm) with a spatula, which was followed by drying at 80 °C for 12 h. The total covering surface area of the active substance on the electrode was 1×1 cm², and the total mass of it was around 1 mg cm^{-2} . All electrochemical analyses were operated on an electrochemical analyzer (CHI 660 E) and were performed in a typical three-electrode setup. Pt wire and Ag/AgCl electrode were used as the counter and the reference electrodes, respectively. The as-prepared electrode was used as the working electrode. CV, GCD and EIS studies were conducted in 1 M H₂SO₄ solution. The EIS spectra were fitted by ECLab software.

The specific capacitance value of the prepared electrode is calculated according to CV curves using the following Equation (1), $^{[49]}$

$$C_{\rm s} = (\int dV) / (vmV) \tag{1}$$

where C_s is the specific capacitance (F g⁻¹), *I* denotes the current density (A g⁻¹), *v* is the scan rate (mV s⁻¹), *m* is the mass of active substance on current collector (g) and *V* is the potential window (V).

The specific capacitance value can be also obtained from the discharge curves by Equation (2), $^{\rm [50]}$

$$C_{\rm s} = (I\Delta t)/(m\Delta V) \tag{2}$$

where *I* refers to the current density (A g⁻¹), Δt is the discharging time, ΔV denotes the potential window (V) and *m* also expresses as the mass of the active substance on current collector (g).

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.202000676.

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