

## Electrochemical Capacitors Based on Nitrogen-Enriched Cobalt (II) Phthalocyanine/Multi-walled Carbon Nanotube Nanocomposites

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A nitrogen-enriched metallophthalocyanine, Cobalt (II) tetrapyrazinoporphyrazine (CoTPyzPz), modified with acid or phenylamine functionalized multiwalled carbon nanotubes (MWCNTaf and MWCNTPhNH<sub>2</sub>) have been studied for application as an electrochemical capacitor in H<sub>2</sub>SO<sub>4</sub>. Both MWCNTaf/CoTPyzPz and MWCNTPhNH<sub>2</sub>/CoTPyzPz gave superior specific capacitance of 1984 and 2028 F.g<sup>-1</sup> respectively. This high capacitance is interpreted in terms of protonation and deprotonation of the porphyrazine macrocycle.

### Introduction

Energy storage devices (ESD), more particularly electrochemical capacitors (ECs) have attracted a considerable interest recently in the world. (ECs) have shown to be desirable ESD as compared to batteries and conventional capacitors for application in high power demand technology. ECs have higher specific power than batteries and higher specific energy than conventional capacitors (1). ECs have superior cycle life performance as compared to batteries and greater energy density than conventional capacitors (2). ECs which are commonly referred to as supercapacitors, double layer capacitors, supercapacitors or ultra capacitors store charge through non faradaic processes (double layer capacitance) and/or non faradaic processes (pseudo-capacitance).

Various carbon materials such as carbon nanotubes (CNTs) and activated carbons (ACs), because of their high surface area have been widely used as electrode materials for electrochemical double layer capacitors (3, 4). Higher surface area is a desirable property for ECs which utilises electro-chemical double layer mechanism for energy storage. Ruthenium oxide (RuO) has been found to be an excellent electrode capacitive material for pseudo-capacitance (5). Due to the high cost and the toxicity of Ruthenium oxide, more metal oxides such as MnO<sub>2</sub> (6), NiO (7), Co<sub>3</sub>O<sub>4</sub> (8), Fe<sub>3</sub>O<sub>4</sub> (9), SnO<sub>2</sub> (10) and V<sub>2</sub>O<sub>5</sub> (11) have been explored as capacitive materials. The study of these metal oxides was an attempt of finding a suitable electroactive material that is chemically and physically stable.

Recently composite materials such as SWCNT-Co<sub>3</sub>O<sub>4</sub> (12), NiOBCPPc-SWCNT-phenylamine (13) and MWCNT-poly-NiTAPc (14) have been studied. CNTs have been found to be good support material for electroactive materials due to their mechanical strength and open tubular network (4). CNTs have been found to be easily integrated with phthalocyanine and porphyrins frameworks through  $\pi$ - $\pi$  interactions due to the delocalized  $\pi$

electrons that each molecule possesses (15-20). The inclusion of CNTs in the composites was reported to have enhanced capacitive behaviour of the composite materials (12-14). The integration of CNTs with metallo-phthalocyanine (MPc) has been found to be suitable for different applications (21-24).

Metalloporphyrazine (MPz) complexes are aza-analogs of phthalocyanines (Pcs) (25). It has been reported that porphyrazine (Pz) molecule is more electronegative than Pc due to eight nitrogens in its outer macrocyclic system and this makes the Pz molecule to be a better  $\delta$  donor and  $\pi$  acceptor (26-28). MPz complexes are known to have interesting properties which makes them utilized for several applications such as oxygen reduction, oxidation of hydrazine, photodynamic-therapy, solar cells, electrochromic devices and gas sensing (29, 30). In this study, we report for the first time, the supercapacitive behaviour of nitrogen-enriched metallophthalocyanine, cobalt (II) tetrapyrizinoporphyrazine (CoTPyzPz) integrated with two types of functionalized MWCNT, namely the acid functionalized and phenylamine functionalized MWCNTs. The choice of these materials for this study was motivated by the reports that nitrogen functionalities on nitrogen doped carbon nanotubes enhance capacitive behaviour.

## Experimental

Multi-walled carbon nanotubes (MWCNT, Nanolab, purity 95%, length 5-10 microns, diameter  $15 \pm 5$  nm) were acid functionalized by following established methods and they are herein referred to as MWCNT acid functionalized (MWCNTaf) (31, 32). MWCNTs were also phenylamine functionalised by using a procedure based on diazonium reactions developed by Bahr et al (33).

Field emission scanning electron microscopy (FESEM) analysis was carried out using a JEOL JSM-2010 operating at an accelerating voltage of 2.00kV. Microstructure analyses were also carried out by transmission electron microscope (TEM). Thermogravimetric analysis (TGA) of the composite materials was carried out with a Mettler Toledo A851 system at a heating rate of  $10^\circ\text{C}/\text{min}$  under air flow. Fourier transform infrared spectroscopy (FTIR) spectra were measured using a Perkin Elmer spectrum RX I FTIR spectrometer with pure anhydrous potassium bromide (KBr) as the background. Sample pellets were made from mixture of active material and KBr (1% of material in KBr).

The electrochemical tests were performed at room temperature in a three conventional electrode cell controlled by PGSTAT 302 (Eco chemie, Utrecht, The Netherlands) using general purpose electrochemical systems data processing software (GPES, software version 4.9). A Ag/AgCl, sat'd KCl and platinum wire and were served as reference and counter electrodes respectively. A custom built basal plane pyrolytic graphite disk electrode (BPPGE, Le Carbone, Sussex, UK 5.0 mm diameter) was used a working electrode. The electrolytes used were 1.0 M  $\text{H}_2\text{SO}_4$  and 1.0M  $\text{Na}_2\text{SO}_4$  solutions. A copper wire inserted into the disk held with conducting silver varnish (Kemo® Electronic, Germany) was used to maintain an electrical contact. Electrochemical impedance spectroscopy (EIS) measurements were performed with Autolab Frequency Response Analyser (FRA) software between 100 kHz and 10 MHz using a 5mV rms sinusoidal modulation. Electrolytes were deaerated with nitrogen for 5min before electrochemical measurements.

BPPGE surface was first cleaned by gentle polishing on a NORTON carborundum paper (12C, P1200), then exfoliated with a masking tape and lastly cleaned in acetone. The cleaned BPPGE was modified by drop dry method with the materials (MWCNTaf, MWCNTPhNH<sub>2</sub>, CoTPyzPz, MWCNTaf/CoTPyzPz and MWCNTPhNH<sub>2</sub>/CoTPyzPz. A 40 $\mu\text{L}$  of modifier solution (2mg of MWCNTaf/CoTPyzPz in 2mL DMF) was drop cast onto a cleaned BPPGE

surface and dried in an oven at 30°C for 30 min. The modified BPGGE was allowed to cool to room temperature before use.

## Results and Discussion

Figure 1 shows typical SEM images of MWCNTaf (i), MWCNTPhNH<sub>2</sub> (ii) and MWCNTaf/CoTPyzPz (iii). The MWCNTs wrap themselves around the CoTPyzPz particles, such connectivity between the MWCNTs and CoTPyzPz macrocycles should enhance the conductivity of the composites.

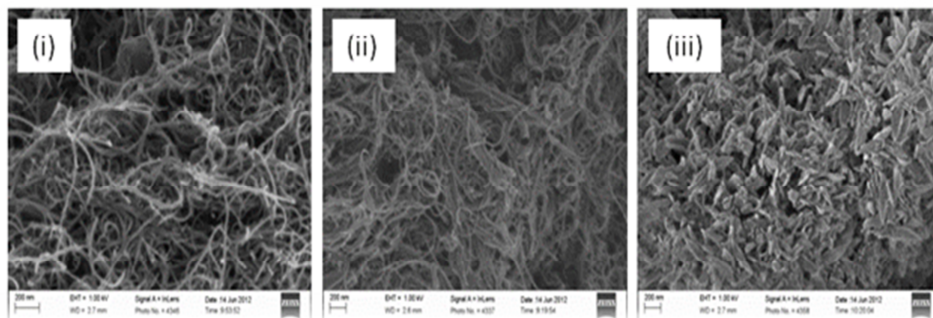


Figure 1: Typical FESEM of (i) MWCNTaf, (ii) MWCNTPhNH<sub>2</sub>, and (iii) MWCNTaf/CoTPyzPz.

The capacitance of the electrode materials (MWCNTs, CoTPyzPz and composites) were studied using cyclic voltammetry at 10 mV.s<sup>-1</sup>. Figure 2 shows the cyclic voltammograms of all the materials in 0.1 M Na<sub>2</sub>SO<sub>4</sub> (i) and 0.1 M H<sub>2</sub>SO<sub>4</sub> which have deviated from a rectangular shape which suggests that the composites and CoTPyzPz materials are pseudocapacitive. Between 0 and -0.2 V, well defined peaks are observed which are attributable to the protonation and deprotonation of the composites and CoTPyzPz only in H<sub>2</sub>SO<sub>4</sub> electrolyte. It has been reported that azomethine nitrogens in phthalocyanines and porphyrazines can be protonated and deprotonated (34). From our experiments it has been observed that the cyclic voltammograms of these materials between 0V and 0.8V do not show this phenomenon. Protonation and deprotonation of the materials seems to be enhanced supercapacitance and this phenomenon is greatly increased by the introduction of the MWCNTs (figure 2). Current separation of the peaks between 0V and -0.2v is bigger in the composites as compared to CoTPyzPz alone.

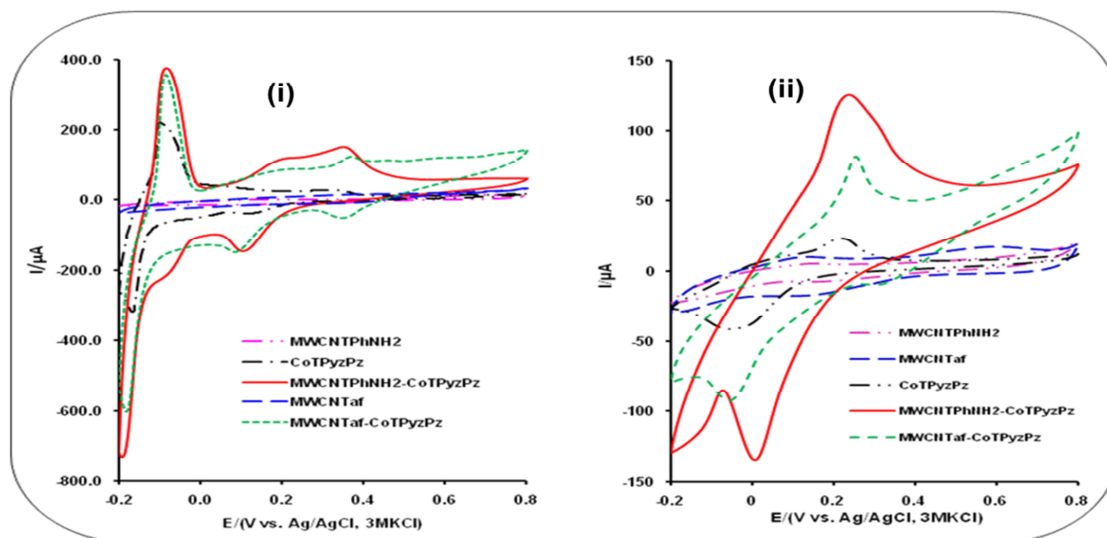


Figure 2: Comparative cyclic voltammograms of various electrodes in (i) 1.0 M H<sub>2</sub>SO<sub>4</sub> electrolyte and (ii) 1.0M Na<sub>2</sub>SO<sub>4</sub> at a scan rate of 10mVs<sup>-1</sup>.

Figure 3 and 4 show the charge-discharge profiles of all the materials. The curves for CoTPyzPz, MWCNTPhNH<sub>2</sub>/CoTPyzPz and MWCNTaf/CoTPyzPz showed that potential is non-linearly dependent on time. This confirms the observation of the CVs that the storage mechanism is largely pseudocapacitive. The specific capacitance (C<sub>sp</sub>) of the electrodes was calculated from the following relationship:

$$C_{sp} = \frac{I \times \Delta t}{\Delta V \times m} \quad [1]$$

where, I is the discharging current applied (A), Δt is the discharging time (s), m is the mass of the active electrode (g) and ΔE is the discharge voltage difference. From the results it was found that MWCNTPhNH<sub>2</sub>/CoTPyzPz displayed the highest specific capacitance of 597 F.g<sup>-1</sup> and 2018 F.g<sup>-1</sup> in 1.0 M Na<sub>2</sub>SO<sub>4</sub> and 1.0 M H<sub>2</sub>SO<sub>4</sub> respectively. The C<sub>sp</sub> values for MWCNTaf/CoTPyzPz are slightly lower than of MWCNTPhNH<sub>2</sub>/CoTPyzPz composite. It was found that in an acidic electrolyte, the C<sub>sp</sub> of MWCNTPhNH<sub>2</sub>/CoTPyzPz is 72, 13 and 5 times the C<sub>sp</sub> of MWCNTPhNH<sub>2</sub>, MWCNTaf and CoTPyzPz respectively. The incorporation of the conductive MWCNTs enhances capacitance dramatically both in Na<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>. This confirms the observation seen in cyclic voltammetry where much energy storage happens between 0 and -0.2V. The extraordinary increase in C<sub>sp</sub> of the composites can be due to increased surface area, wettability of the electrodes by the incorporation of functionalised MWCNTs and the protonation and deprotonation of the macrocycle.

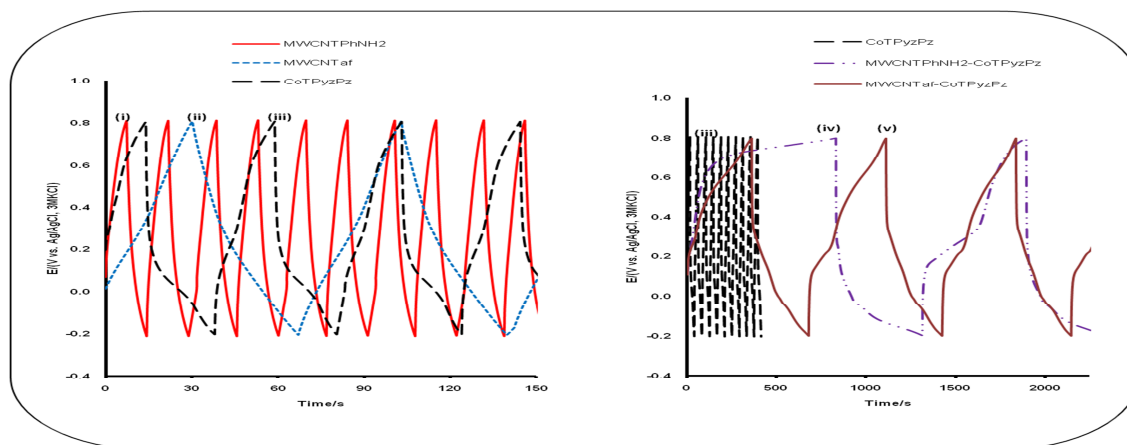


Figure 3: Charge-Discharge (C-D) curves of (i) MWCNTPhNH<sub>2</sub>, (ii) MWCNTaf, (iii) CoTPyzPz, (iv) MWCNTPhNH<sub>2</sub>/CoTPyzPz (v) MWCNTaf/CoTPyzPz at 1A/g in 1.0 M Na<sub>2</sub>SO<sub>4</sub>

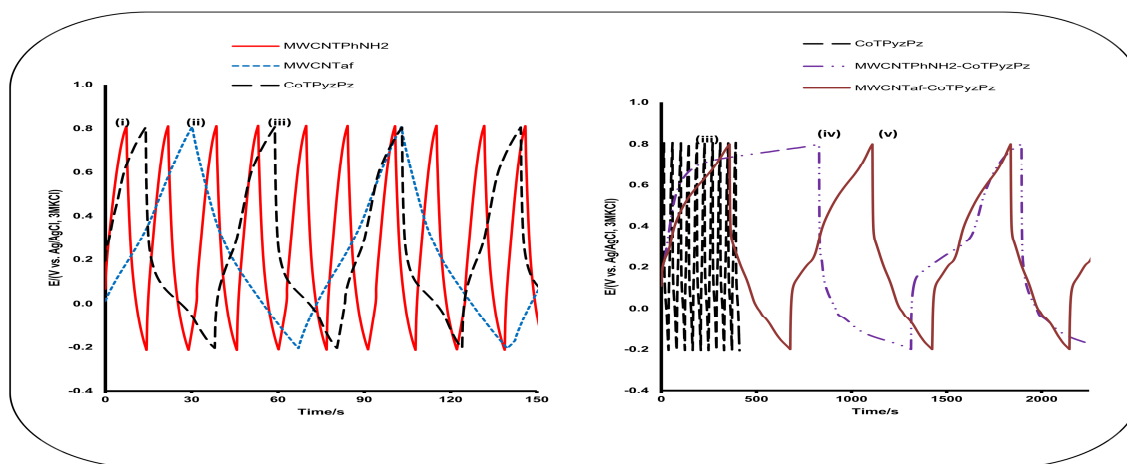


Figure 4: Charge-Discharge (C-D) curves of (i) MWCNTPhNH<sub>2</sub>, (ii) MWCNTaf, (iii) CoTPyzPz, (iv) MWCNTPhNH<sub>2</sub>/CoTPyzPz (v) MWCNTaf/CoTPyzPz at 1A/g in 1.0 M H<sub>2</sub>SO<sub>4</sub>

**TABLE I.** Supercapacitive behaviour parameters of MWCNTPhNH<sub>2</sub>, MWCNTaf, CoTPyzPz, MWCNTPhNH<sub>2</sub>/CoTPyzPz and MWCNTaf/CoTPyzPz at a current density of 1A.g<sup>-1</sup>

Electrode	Csp in 0.1M Na <sub>2</sub> SO <sub>4</sub> /(F.g <sup>-1</sup> )	Csp in 0.1M H <sub>2</sub> SO <sub>4</sub> /(F.g <sup>-1</sup> )
MWCNTPhNH <sub>2</sub>	8	27
MWCNTaf	37	154
CoTPyzPz	27	374
MWCNTPhNH <sub>2</sub> /CoTPyzPz	597	2028
MWCNTaf/CoTPyzPz	376	1984

The wettability of the electrodes leads to greater accessibility of the electrode surface by the ions of the electrolyte. Due to the basicity of the porphyrine molecule due to the presence

of the azomethine and pyrazine nitrogen atoms, protonation and deprotonation is more favourable in an acidic electrolyte (35).

From charge discharge experiments of MWCNTaf/CoTPyz electrode (figure 5) in 1.0M H<sub>2</sub>SO<sub>4</sub> and 1.0M Na<sub>2</sub>SO<sub>4</sub> at different current density, it was found that C<sub>sp</sub> decreases as current density increases. The specific power and specific energy were calculated using the equation 2 and 3 respectively:

$$SP(kW.kg^{-1}) = \frac{I \times \Delta t}{m} \quad [2]$$

$$SE(Wh.kg^{-1}) = \frac{I \times \Delta t \times \Delta E}{m} \quad [3]$$

The specific power obtained for MWCNTaf/CoTPyzPz obtained was 952 W.kg<sup>-1</sup> and 834 W.kg<sup>-1</sup> in 1.0 M H<sub>2</sub>SO<sub>4</sub> and 1.0 M Na<sub>2</sub>SO<sub>4</sub> respectively and while the specific energy was 250 Wh.kg<sup>-1</sup> and 36 Wh.kg<sup>-1</sup> in 1.0 M H<sub>2</sub>SO<sub>4</sub> and 1.0 M Na<sub>2</sub>SO<sub>4</sub> respectively. The inset in figure 5 shows the charge discharge profile of 1000 cycles.

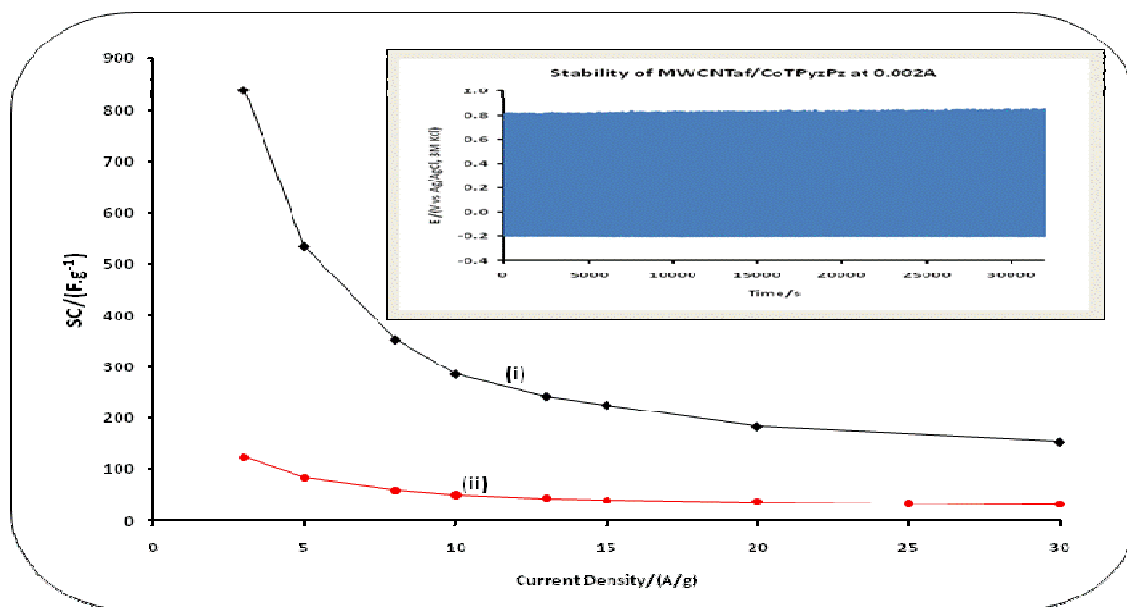


Figure 5: Specific capacitance of MWCNTaf/CoTPyzPz at different current density in (i) 1.0 M H<sub>2</sub>SO<sub>4</sub> and (ii) 1.0 M Na<sub>2</sub>SO<sub>4</sub>. Inset shows charge discharge stability of MWCNTaf/CoTPyzPz

## Conclusions

This study demonstrates that MWCNTs/CoTPyzPz composites are promising electrode materials for supercapacitor applications in aqueous electrolytes. The MWCNTs/CoTPyzPz electrode materials have shown a remarkable protonation and deprotonation process that dominates the energy storage mechanism in these materials. On the basis of the results, the incorporation of MWCNTs into CoTPyzPz macrocycle remarkably enhanced the electrochemical capacitance. Interestingly, even at a higher current density of 30 A.g<sup>-1</sup>,



MWCNTaf/CoTPyzPz gave a specific capacitance of 154 F g<sup>-1</sup> and 32 F g<sup>-1</sup> in 1.0 M H<sub>2</sub>SO<sub>4</sub> and 1.0 M Na<sub>2</sub>SO<sub>4</sub> electrolytes, respectively.

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