



Electrochemical Capacitive Behaviour of Tetra (Phenoxymethyl) benzylamine Nickel(II) Phthalocyanine Composites With MWCNT

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Abstract

In this work we are synthesise tetra (phenoxymethyl) benzylamine Nickel (II) phthalocyanine and also make their composite with MWCNT. The prepared compounds can be characterized by IR, UV, XRD and TGA. So that we can have confirmation of formation of synthesised compounds. Electrochemical studies can be done by the Cyclic voltammetry method. This method of analysis is provided with three electrode system. From this method we got the supercapacitance value for the NiTPMBPc and their composite are 54.62 Fg⁻¹ and 76.11 Fg⁻¹ respectively. The results can show that the supercapacitance can be enhanced by making their composites by carbon materials like MWCNT. The results can be show that these are good for supercapacitor.

Keywords: Phthalocyanine, Cyclic voltammetry, Xrd, Microwave method, Electrochemical studies.

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1. Introduction

Nowadays the researchers are eagerly to find the efficient energy storage devices (ESD), in this context electrochemical capacitors (ECs) have attracts more. Appreciable power densities are observed in ECs than the batteries and have more energy density in ECs than the conventional capacitors. Also ECs are having better cyclic stability over the batteries and the conventional capacitors[1]. ECs are commonly referred as ultracapacitors or supercapacitors or double layer capacitors. The charge can stored in these ESD and charge storage is done by faradaic or non-faradic process. Double layer capacitance is achieved by faradic process and pseudo-capacitance is achieved by non-faradaic process[2]. ECs are utilised in enormous applications where require large amount of energy in few seconds, like escalators, uninterrupted power supplies, emergency doors, in vehicles and in metro trains[3]. In particular the supercapacitors built up with three components they are two electrodes separated by an electrolyte by a separator[4-6]. The electrodes are made up of with active carbon materials like carbon nanotubes, carbon aerogels, carbon templates, active carbon fibres[7-15]. In this way the electrolyte got more importance. The electrolytes may be organic, aqueous and polymer gel electrolyte[16-19]. The carbon material can exhibits tremendous capacitances due to its high surface area, better thermal stability and economically low cost with better electrical conductivity[20-22]. By the above properties of carbon materials we can say that these carbon materials are suitable for supercapacitors.

Metal Phthalocyanines (MPs) are comes under the class of macrocycles with four isoindole units bonded to metal atom. MPs are attracted towards the electrochemical

applications like sensors, electrocatalysis, supercapacitors etc., they show unique properties like redox nature, physico-chemical properties with high charge mobility[23-24]. The central metal rings with metal centres can enhance their electron transfer leads to increase in energy storage systems. Only a few metal based Phthalocyanines with cobalt, iron, copper and nickel are examined as electrode materials for electrochemical capacitor applications[20-25]. Among them the nickel Phthalocyanines and its derivatives are chemically and thermally stable electrode materials which shows outstanding performance cyclic stability for symmetric capacitors[26-28], MPCs for electrochemical sensing applications [29-47].

Multiwalled carbon nanotubes (MWCNTs) are having large surface area, thermal stability and having better electrical conductivity. These MWCNTs are composite with the Phthalocyanines are also increases their activity. The supercapacitive properties are also increased by making composites of Phthalocyanine with MWCNT. Hence in this study we successfully synthesised tetra (phenoxyethyl) benzylaminenickel(II) Phthalocyanine by microwave method and make composite with MWCNT by employed mechano chemical method. Prepared composites are employed for study the supercapacitive behaviour using cyclic voltammetry measurements and cyclic stability is determined by the galvanostatic charge and discharge method.

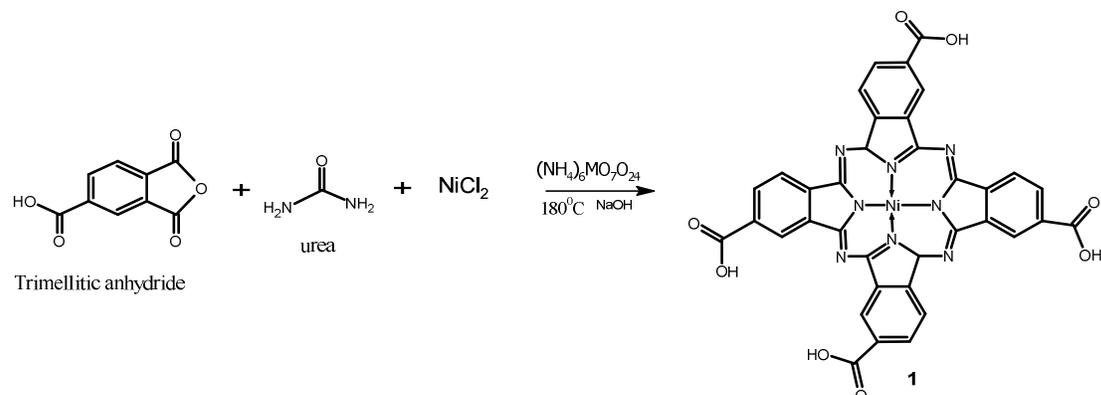
2. Experimental details

2.1. Materials

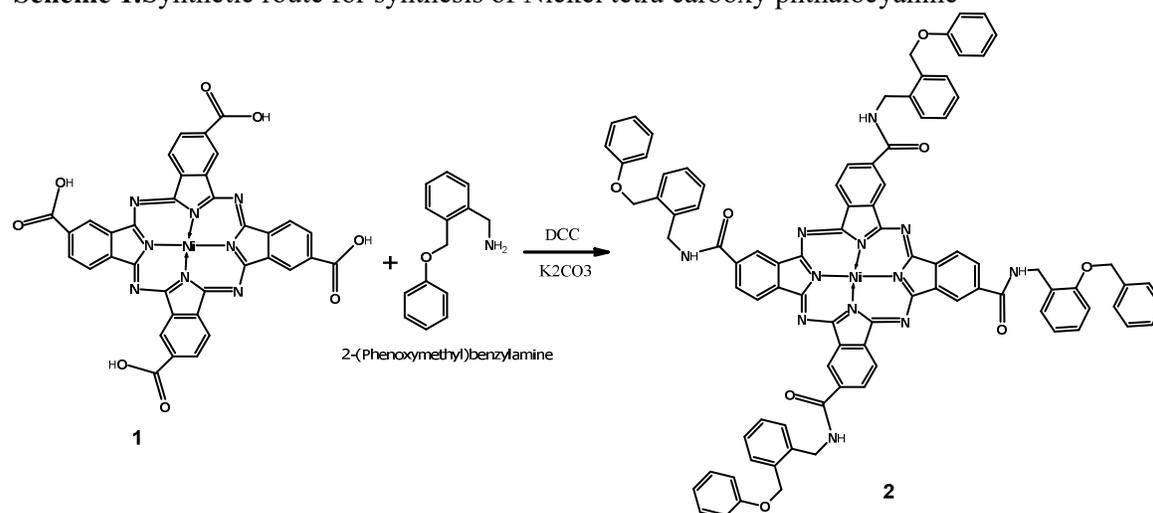
1,2,4- Benzene tri-carboxylic anhydride i.e. trimellitic anhydride (TMA), Multiwalled carbon nanotubes (MWCNT), (phenoxyethyl) benzylamine was purchased from sigma Aldrich (India), hydrochloric acid (HCl), dimethyl formamide (DMF), sodium hydroxide (NaOH) pellets, N,N' dicyclo hexyl carbamide (DCC), urea, ammonium ferrous sulphate (FAS), Nickel chloride (NiCl_2) purchased from spectrochem chemicals India.

2.2. Synthesis of tetracarboxy nickel (II) phthalocyanine (NiTCPC)

The tetracarboxynickel(II) phthalocyanine is prepared by the microwave synthetic method reported in the literature [48, 49] with little modification as explained in the **scheme 1.A**. A mixture of TMA 0.4g (10mmol), 0.1g of nickel chloride (NiCl_2) (2mmol), 16g of urea (130mmol), 0.13g of FAS (5.4mmol) and 0.1 g of ammonium hepta hydrate (as a catalytic amount) were ground together to make fine powder using mortar and pestle for about 5 min. the finely powdered homogeneous powder is transferred to 250ml glass beaker and kept in domestic oven. Gradually rise the temperature from lower to higher. Heat the reaction mixture for 1 min and take out the glass beaker and stir and mix the reaction mixture then kept in oven. The same procedure should be repeated for 20 min. finally a green coloured complex is formed. The product can be treated with double distilled water, ethanol, dilute NaOH, dilute HCl filter and dried in an oven at 50°C for 15 Hours, nearly 80% is obtained. IR (KBR); in cm^{-1} ; 3380, 1691, 1629, 1574, 1423, 1091, 755, 662, UV-Vis (DMSO); λ in nm; 324, 656 (dimer), 650 (monomer); Elemental analysis ($\text{C}_{46}\text{H}_{26}\text{N}_{10}\text{NiO}_{14}$) found C 55.0, H is 2.6, N is 14.5 O is 5.83; calculated; C is 55.2, H is 2.5, O is 5.8 and N is 14.3.



Scheme 1. Synthetic route for synthesis of Nickel tetra carboxy phthalocyanine



Scheme 2. Synthetic route for the synthesis of tetra (phenoxyethyl) benzylamine nickel (II) phthalocyanine.

2.3. Synthesis of tetra (phenoxyethyl) benzylamine nickel(II) phthalocyanine (NiTPMBPc)

NiTPMBPc can be synthesised by (Scheme 2). The method reported in the literature [50-53]. A finely ground the mixture NiTCpC (9mmol), small amount of K₂CO₃ and (phenoxyethyl) benzylamine is made to dissolve in 25ml of DMF in RB flask followed by adding a catalytic amount of N, N' DCC stirred for 36 Hours at room temperature. The dark green coloured product is separated by using hot water and hexane. The resultant product was obtained and is dried using P₂O₅ in desiccator. NiTPMBPc was prepared yielding 79%; Anal. For NiTPMBPc with molecular weight 1528.29 C₉₂H₆₈N₁₂NiO₈ calc. (%) C- 72.25. H- 4.42, O – 8.34, N – 10.95, Ni – 3.52; found: C- 72.2. H- 4.4, O – 8.3, N – 10.9, Ni – 3.5; UV – VIS (H₂SO₄) λ_{max}(nm): 331, 432, 611, and 615. IR absorption bands (KBr cm⁻¹): 762, 843, 935, 1057, 1113, 1142, 1167, 1222, 1271, 1312, 1395, 1410, 1516, 1643, 1661 and 3344. , UV-Vis (DMSO); λ in nm 330, 670 (dimer), 651 (monomer).

2.4. Preparation of multiwall carbon nanotube (MWCNT) composites with NiTPMBPc

Take a homogeneous solution of 0.5 g of NiTPMBPc with 4 ml of ethanol in agate mortar to that add 0.1 g of MWCNT is added, agitated for about 1 Hour. Resultant dried product is removed from the agate mortar after 1 hour, kept for sintering at 400⁰C for 40 min results composites of NiTPMBPc with MWCNT. The resultant product can be confirmed by FTIR and XRD. Obtained NiTPMBPc/MWCNT composites make a solution with 10 ml DMF and

kept for sonication for about 30 min. by that solution take drop using a micropipette and placed on glassy carbon electrode (GCE). The drop should be covering the surface of the electrode. The drop should be uniformly covering the surface of the GCE and kept the electrode for 12 Hour.

2.5. Preparation of modified electrodes

The surface of the GCE was cleaned by deionised water thoroughly, followed by polished the surface to remove the dust particles or any other composites using 0.5 mm alumina slurries using polishing pad, then the surface of the GCE is rinsed thoroughly using double distilled water and the electrode is kept for sonication for about 5 min in acetone then in water, at last kept for drying in air. Prepared NiTPMBPc/MWCNT shall be coated on the surface of the GCE by drop mount method. Now the electrode is ready for the analysis.

2.6. Characterization

The electronic spectral studies done by the instrument shimadzu UV-550 spectrophotometer. Vibrational spectral studies done by perkinelmerspectrum 100 FTIR spectrometer using KBr pellet qualitatively. The powder X-Ray (PXRD) analysis done with room temperature of 26⁰C on a Bruker Advanced Cu Ka Radiation Source. The thermal studies for the synthesised complex and the composites were done with STA000 instrument between the temperature ranges of 30⁰C to 800⁰C, electrochemical measurements were done by using CH instruments electrochemical analyser CH1620E, is fitted with three electrodes among them one is platinum wire as auxiliary electrode. Ag/AgCl saturated with 3M KCl as reference electrode and GCE is a working electrode.

3. Results and discussion

3.1. UV Visible spectroscopy

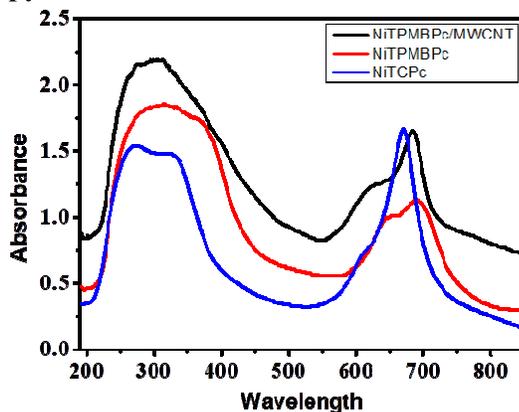


Figure 1. UV-visible absorption spectrum of A) NiTCPc, B) NiTPMBPc and C) MWCNT-NiTPMBPc

Figure 1 describes the comparative UV-visible spectra for NiTCPc, NiTPMBPc and NiTPMBPc/MWCNT in DMSO. The observed spectra proclaimed the characteristic Q-band typical for the different substituted phthalocyanine.

The NiTCPc complex shows two absorption bands at 343 nm (B-band) and 678 nm (Q-band), while for NiTPMBPc, the B-band and the Q-band appears at 360nm and 696 nm, respectively. The two peak bands at 435 nm and 495 nm observed for the NiTPMBPc complex is typical of a low spin six coordinate Ni²⁺Pc species and are usually associated with

Ni^{2+} to ligand transfer transition [54, 55]. Hence its presence is a good indication that the central metal ion remains in the +2 oxidation state. Both B and Q bands of the NiTPMBPc complex slightly shifted to longer wavelength when compared to the NiTPMBPc compared to the NiTCPc complex, such a slight red shift is an indication that the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the NiTPMBPc is narrower than that of NiTCPc complex. In the NiTPMBPc-MWCNT spectrum, the Q Band appears as one very broad aggregated from peak at ~ 650 nm; this also provides evidence for the presence of composites of MWCNT.

3.2. FT-IR Spectral study

To identify the chemical composition of the samples, the FT-IR test is performed. The FT-IR spectra for NiTCPc, NiTPMBPc and NiTPMBPc/MWCNT are represented in the Fig. 2. The similar functional groups are present in these compounds so obtained spectra are also similar. The band at 1652 cm^{-1} was belonged to C=O, the 1600-1300 bands are related to $\nu(\text{C-C})$ benzene ring skeletal stretching, the 1300-1000 cm^{-1} , bands are appeared due to $\beta(\text{C-H})$ in plane bending, and the 700-800 cm^{-1} band corresponded to the $\gamma(\text{C-H})$ out of the plane bending. . In the Fig.2a.curve the peak at 2978 cm^{-1} corresponding to O-H is disappeared and in the Fig. 2b. Appearance of new peak at 3412 cm^{-1} , this confirms the formation of NiTPMBPc. In the Fig.2c the NiTPMBPc/MWCNT is exactly same and overlapping with NiTPMBPc curve with a peak at 3443 cm^{-1} and this confirms composites.

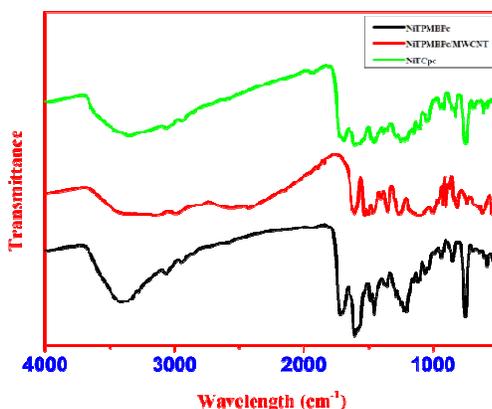


Figure 2. FT-IR graphs of NiTCPc, NiTPMBPc and NiTPMBPc/MWCNT

3.3. Powder X Ray Diffraction

The powder X-Ray Diffraction (XRD) patterns of the NiTCPc, NiTPMBPc and NiTPMBPc/MWCNT is as shown in the fig 3. The diffraction peak for NiTCPc is inset in the Fig 3a. The diffraction peaks of the NiTPMBPc/MWCNT (Fig. 3c) were broad and weak, signifying a small crystal size or poor crystallinity of NiTPMBPc in NiTPMBPc/MWCNT hybrid materials. Especially, related to pure NiTPMBPc (Fig. 3b), the characteristic peaks of the NiTPMBPc/MWCNT got weak because the NiTPMBPc particles are well agglomerated on the surface of the MWCNTs. Therefore, the XRD patterns give evidence that the composite NiTPMBPc/MWCNT were prepared successfully.

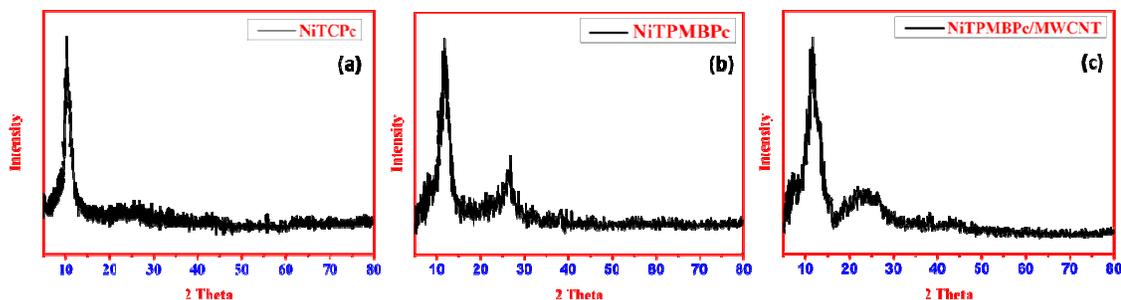


Figure 3. XRD graphs of (a) NiTCPc, (b) NiTPMBPc and (c) NiTPMBPc/MWCNT

3.4. Thermal studies

The thermal studies of NiTCPc, NiTPMBPc and NiTPMBPc/MWCNT determine the thermal stability and the decomposition behaviour of the complexes at different temperatures inset in the Fig.4. The decomposition of the complexes takes place in three steps. In the first step the decomposition takes place at 100⁰C, due to the moisture present on the surface of the compound has been evaporated. In the second step maximum weight can be reduced at 320 to 540⁰C for NiTCPc, NiTPMBPc and NiTPMBPc/MWCNT. The curve for NiTCPc is showed stable upto 380⁰C NiTPMBPc is stable upto 400⁰C and the NiTPMBPc/MWCNT is stable at 480⁰C. In the final step the both the complexes are in the oxidation sphere so these are formed the product as NiO. By these curves we can clearly understand that both the complexes are stable upto 400⁰C.

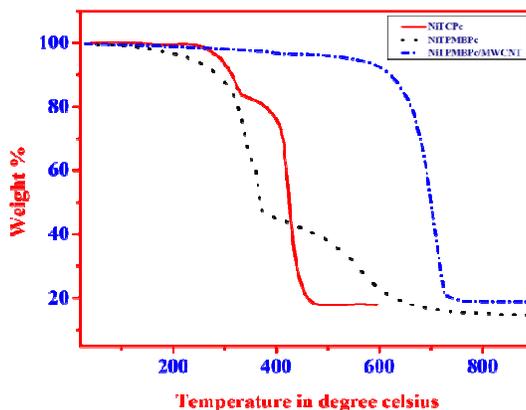


Figure 4. Thermograms of NiTCPc, NiTPMBPc and NiTPMBPc/MWCNT

3.5. Cyclic voltammetry experiments

Figure 5 explains the cyclic voltammetry curves results at scan rate 0.1 mVs⁻¹ to 0.5 mVs⁻¹ in 1 M Na₂SO₄ at (i) NiTPMBPc/GCE and (ii) NiTPMBPc/MWCNT/GCE. The obtained cyclic voltammograms are nearly distorted rectangular in shape. In the potential range between -0.4 to 1.2 for NiTPMBPc/GCE and -0.5 to 1.5 for NiTPMBPc/MWCNT/GCE region with a weak redox process. The CVs clearly indicate the overall electrochemical process is a combination of double layer capacitance (non faradaic) and pseudocapacitance (faradaic) processes. Fig. 5 shows the CVs pattern at different scan rate for NiTPMBPc/MWCNT/GCE increasing scan rate, the CV pattern maintain their shape of the curve but with increasing magnitude [56, 57]. Their observations suggest that (i) the electrode is charged and discharged at pseudo constant rate and (ii) the diffusion ion from the electrolyte into the pores is easily accessible irrespective of the potential scan rate. Similar trend were also observed for NiTPMBPc/GCE. The capacitive behaviour is examined in detail using more reliable galvanostatic charge-discharge strategy.

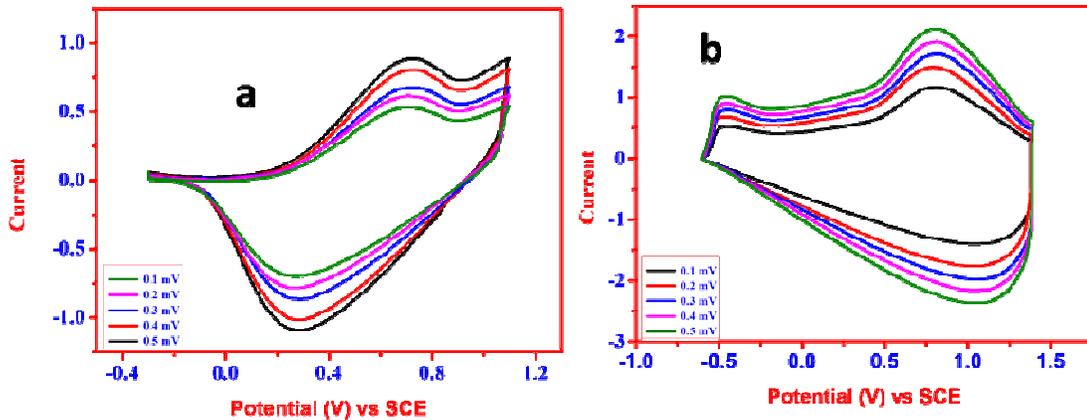


Figure 5. The CV Curves of a) NiTPMBPc/GCE and b) NiTPMBPc/MWCNT/GCE

The specific capacitance (C) was calculated by the discharge curve employing the equation as below

$$\text{Capacitance } C = \frac{\int Idv}{s \times 2 \times V \times m} \text{-----} \rightarrow (\text{Eq.1})$$

Where $\int Idv$ = Area of the cyclic voltammogram, S is scan rate, V is the voltage window and mass of active material in grams and C is the capacitance in F/g. The obtained maximum specific capacitance values for (i) NiTPMBPc/GCE and (ii) NiTPMBPc/MWCNT/GCE 54.62 F/g and 76.11 F/g at Scan rates as 0.1 mV. The Energy density and power densities are most significant for analysing the electrochemical behaviour. The Energy density can be calculated by the equation (A) and for the power density equation (B) can be consider.

$$E = \frac{1}{2} CV^2 \text{-----} \rightarrow (\text{A})$$

$$P = \frac{E}{t} \text{-----} \rightarrow (\text{B})$$

Where E be the Energy density (Wh/kg), C is the capacitance (F/g), V is the charge-discharge potential, P is the power density (kW/kg) and t is the discharging time in seconds. the energy density for NiTCPMBPc/GCE and NiTCPMBPc/MWCNTs/GCE 61.74 kW/kg and 86.12. Simultaneously the calculated power density increases for NiTCPMBPc/GCE and NiTCPMBPc/MWCNTs/GCE 1.47 kW/kg and 0.038 kW/kg. Higher the energy density of 86.12 Wh/g was achieved for NiTCPMBPc/MWCNTs/GCE implying its potential application as high energy storage materials towards electrochemical supercapacitor applications.

4. Conclusion

In brief, this work involves the conventional method for the synthesis of NiTCPMBPc, the doping of MWCNT on the synthesised phthalocyanine has been done and confirmed the structure by UV, FTIR and XRD analysis. The thermal studies gives the compound is stable upto 400°C. The electrochemical studies done by using CV and calculate the specific capacitance at different scan rate. The maximum specific capacitance value (i) NiTPMBPc/GCE and (ii) NiTPMBPc/MWCNT/GCE 54.62 F/g and 76.11 F/g respectively at Scan rates as 0.1 mV. This indicates potential application as electrode materials for energy storage application as well as other applications where high surface area and conductivity is desirable. Finally the carbon nanotubes are improve the supercapacitor properties so that this electrode can be used as a promising candidate for positive electrode in supercapacitor devices.

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