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# Electropolymerization of palladium tetraaminephthalocyanine: Characterization and supercapacitance behavior

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ABSTRACT

The formation of a supramolecular electropolymerized film of a polymeric palladium phthalocyanine on a glassy carbon electrode is reported here. The film was obtained by cycling monomeric palladium tetraaminephthalocyanine in dimethyl sulfoxide in the potential range −0.5 to +1.0 V. The functionalized polymerized film on the electrode was characterized using Raman spectroscopy, X-ray photoelectron spectroscopy and electrochemical methods. A polymeric phthalocyanine film was shown to form by the oxidation of peripheral amino groups. It uniformly and completely covered the electrode surface. The modified electrode surface slightly blocked the reversible redox behavior of a redox probe owing to the thick polymeric film on its surface. The modified electrode showed a redox capacitance of 146 F $g^{-1}$ at 0.27 V in 0.5 M sulfuric acid.

## 1. Introduction

Metal phthalocyanines (MPcs) are of interest to various fields because of their chemical adaptability, architectural flexibility, diverse coordination properties, spectroscopic characteristics, color and stability [1], which give them wide applicability. Different MPc complexes have been presented for use in various applications and functional devices such as organic field effect transistors, sensors, light-emitting devices, information storage, and photovoltaic materials for solar energy conversion [1,2]. They have also been reported for biological uses such as photodynamic therapy and drug delivery [3]. Materials based on phthalocyanine (Pc) have also been widely studied for their excellent catalytic properties, which arise owing to their high degree of electrochemical reversibility and ultra-fast redox changes [1,4–7]. The conductivity of Pc can be enhanced for various applications by the introduction of functional groups and also by polymerization [7–9].

The formation of well-ordered MPc films on various conducting solid substrates is often important to their effective use [7,10]. Electropolymerization is a simple and rapid method of depositing films. It allows the deposition of the film (and its resulting conductivity) to be controlled via the selection of the monomer and/or the potentiometric conditions. If the benzene fragments of Pc ligands are suitably substituted, the Pc can be immobilized on the surface of an electrode by anodic oxidation of the functional groups [11]. Electrochemical cycling can induce the $-NH_2$ groups of Pcs containing amines to undergo anodic oxidation, leading to the electropolymerization of the Pc [11]. The process is presumed to be analogous to the oxidation of aniline in the formation of polymeric aniline (PANI) [12], an electroactive conducting polymer (ECP). However, the conduction in polymerized Pcs differs from that in other (ECP) because it occurs through two electronic subsystems of delocalized charge carriers. These subsystems might arise because of the peculiarities of the anodic doping and the cathodic behavior of the polymeric films and their precursors in solution are similar to those of a redox polymer. Therefore, electropolymerized Pcs can be considered a hybrid class of polymer with the properties of both electron-conducting and redox polymers. Electropolymerized Pcs exhibit redox activity in a wide potential range, and they retain the electrocatalytic features of their precursors. This gives them potential applicability as chemical power sources, supercapacitors, and electrochemical sensors [12]. Pc-modified electrodes for electrochemical sensing have been well reported [7,10,12–14], but the use of these materials as electrochemical power sources is less well explored [15,16].

This work reports the synthesis of a palladium tetraaminephthalocyanine monomer as palladium is known to be a very good

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catalyst in homogeneous and heterogeneous catalysis [17,18]. The monomeric molecule is electropolymerized on a glassy carbon electrode (GCE) as this electrode shows a higher current response than a gold electrode. The electropolymerized film was characterized, and its supercapacitance behavior was analyzed.

## 2. Materials and methods

### 2.1. Materials

Nitrophthalonitrile, $PdCl_2$, sodium sulfide ($Na_2S \cdot 9H_2O$), tetrabutyl ammonium perchlorate (TBAP), urea ($CO(NH_2)_2$), ammonium chloride ($NH_4Cl$), ammoniummolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), ferrocene, sodium hydroxide (NaOH), nitrobenzene ($C_6H_5NO_2$), methanol ($CH_3OH$), ethanol ($C_2H_5OH$), tetrahydrofuran (THF), acetone ($CH_3COCH_3$), dimethyl sulfoxide (DMSO, 98%), phosphate buffer (pH 7.0), hydrochloric acid (HCl), and sulfuric acid ($H_2SO_4$) were from Sigma–Aldrich and used as received. Potassium ferrocyanide ($K_4Fe(CN)_6$) was from Merck Eurolab.

Inlaid glassy carbon (GC) disks of surface area 0.0201 $cm^2$ (BASi) were used as electrodes in the electropolymerization and in subsequent analyses. The GCEs were polished with a polishing cloth (MicroCloth, Buehler) using sequentially 1.0 μm and 0.5 μm alumina. They were then repeatedly washed in water and then in ethanol while being sonicated for 10 min in an ultrasonic bath.

### 2.2. Synthesis of palladium(II) tetraaminephthalocyanines

Palladium tetraaminephthalocyanine (PdTAPc) was synthesized from palladium(II) tetranitrophthalocyanine (PdTNPc) [19], the synthesis of which is briefly outlined below.

#### 2.2.1. Synthesis of palladium(II) tetranitrophthalocyanine (PdTNPc)

A mixture of 4-nitrophthalonitrile (0.039 mol) and $PdCl_2$ (0.01 mol), urea (0.08 mol), $NH_4Cl$ (0.02 mol), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.05 g) were mixed and grounded well. To this mixture nitrobenzene (10 ml) was added and heated slowly to 140 °C. It was further heated to 160 °C and held at that temperature with constant stirring for 3 h under reflux. The solid crude PdTNPc product was purified [19] to obtain a blue–green product. Anal. for PdTNPc, $C_{32}H_{12}N_{12}O_8Pd$: Calc. (%) C, 48.1; H, 1.50; N, 21.04; O, 16.03; Pd, 13.33. Found C, 48.49; H, 1.34; N, 20.79; Pd, 13.56. Electronic absorption, $\lambda_{max}$ (nm): 346, 431, 620, 684. IR absorption bands ($cm^{-1}$): 755(w), 815(w), 845(s), 909(w), 1048(w), 1104(m), 1143(s), 1256 (s), 1330(s), 1405(m), 1437(w), 1523(s), 1605(m). Yield: 85%.

#### 2.2.2. Synthesis of palladium(II) tetraaminephthalocyanine (PdTAPc)

The nitro derivative PdTNPc was reduced using sodium sulfide to give PdTAPc [19]. To a slurry of PdTNPc (2.0 g) in water (50 mL), sodium sulfide nonahydrate (10 g) was added and the mixture was stirred at 50 °C for 5 h. The product was allowed to settle, before purification [19] to a dark blue solid. Anal. for PdTAPc, $C_{32}H_{20}N_{12}Pd$: Calc. (%)C,56.59; H, 2.95; N,24.74; Pd,15.72. Found (%): C,56.16; H, 3.24; N,24.79; Pd,15.84. Electronic absorption, $\lambda_{max}$ (nm): 313,432,648, 724. IR absorption bands ($cm^{-1}$):754(w), 817(m), 868(s), 909(s), 946(w), 1052(w), 1105(m), 1143(s),1255(w), 1334(s), 1408(w), 1516(s), 3215(w), 3334(s). Yield: 78%.

### 2.3. Characterization methods

Elemental analyses for carbon, hydrogen, and nitrogen were conducted using a Vario EL-III CHNS Element Analyzer (Elementar Analysensysteme GmbH). The metal contents of the metal complexes were determined by decomposing a known amount of the complex using a mixture of $H_2SO_4$ and $HNO_3$, followed by careful evaporation and calcinations [20]. UV–VIS spectra were recorded using a Cary 50 (Varian) with DMSO as a blank. Spectra were recorded in the region of 280–800 nm using 0.5 mM complex in DMSO. IR spectra were recorded using a Perkin Elmer Spectrum 100 FTIR spectrometer attached to a Spotlight 400-Perkin Elmer FTIR imaging system in Attenuated Total Reflectance mode with germanium crystal. A confocal Raman spectrometer Senterra R200-L (Bruker) was used to analyze the films on the GCE. Raman spectra were recorded using a 785 nm diode laser with a power of 300 mW at the source. An Olympus microscope (objective lens of 50 × magnification) coupled to the spectrometer was used to visualize the samples and also for microanalysis. The spectrometer was equipped with a thermo-electrically cooled charge coupled device detector (1024 × 256 pixels). Raman spectra of the electropolymerized films on GCEs were recorded in the wave number region 100–1700 $cm^{-1}$. Each spectrum was the result of 15 accumulations of 30 s each.

X-ray photoelectron spectroscopy (XPS) was conducted using an S-Probe monochromated XPS spectrometer from Surface Science Instruments (VG) with an Al Kα X-ray (1486.6 eV) monochromatic source. The take off angle was 45°; the voltage and power of the source were 10 kV and 200 W, respectively. A base pressure of $2 \times 10^{-9}$ mbar was obtained in the measuring chamber; the pass energy was 157.7 eV (resolution stand 4: 0.15 eV). A surface of 250 μm × 1000 μm was analyzed using a flood gun (neutralizer) setting of 0.2 eV. Accumulation was for about 1 h each for the Pd3d, N1s, and C1s spectra.

Cyclic voltammetry was performed using an Autolab potentiostat (PGSTAT 100, Netherlands) with general purpose electrochemical system software. Three-electrode cell systems were tested using a saturated calomel electrode (SCE) as reference with a GC working electrode and a carbon counter electrode. The electrochemical experiments were performed in an inert atmosphere achieved by purging the system with nitrogen gas for 20 min before each experiment. The electrochemical stability of each film was studied by repeatedly scanning the modified electrodes. This electrochemical pre-treatment served to further the removal of any physically adsorbed PdTAPc that may have remained after washing.

The charge transfer behavior of the pristine and the modified GCE was assessed using 1 mM $K_4Fe(CN)_6$ in phosphate buffer. Impedance measurements were conducted using an Autolab (PGSTAT 20, Netherlands) with frequency response analysis software. Measurements were conducted in the frequency range 1 MHz–10 mHz with an amplitude of 5 mV in an electrolyte containing 1 mM $K_4Fe(CN)_6$.

## 3. Results and discussion

The structure of PdTAPc precursor and its transformation to polymeric PdTAPc, poly(PdTAPc) are shown in Scheme 1. The precursor has four amine functional groups at the periphery of the benzene rings. The compound was green in color, planar, and highly stable. It was soluble in dimethyl sulfoxide, dimethyl formamide, pyridine, chloronaphthalene, and sulfuric acid (28N); the resulting solutions each remained stable for more than one week, but the complexes eventually aggregated and precipitated. In the sulfuric acid solvent, protonation of the complexes is likely, which assist solubility of the complexes. The PdTAPc compound is most likely a mixture of various positional isomers as it is very difficult to purify and obtain a single isomer [19].

UV–VIS experiments were performed in dimethyl sulphoxide solvent in the range 280–800 nm (the UV cut-off region for DMSO is 265 nm) for PdTNPc and PdTAPc [19]. The complexes showed peaks in the Q-band region 615–730 nm, responsible for the