One-step oxidation of aniline by peroxotitanium acid to polyaniline–titanium dioxide: A highly stable electrode for a supercapacitor

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ABSTRACT: In this study, to make a stable electrode material for a supercapacitor, we selected a polyaniline and titanium dioxide (TiO_2) hybrid material. Peroxotitanium acid was used to oxidize aniline in the presence of sulfuric acid to a poly(aniline sulfate) salt–titanium oxide composite in one step. IR, X-ray diffraction, and energy dispersive X-ray analysis (EDAX) analyses supported the formation of the composite. The poly(aniline sulfate) salt–titanium oxide composites (50 wt % each) showed an amorphous, flakelike morphology having a conductivity value of 8×10^{-3} S/cm with an excellent yield and stability (300°C).This composite material in the cell configuration showed a specific capacitance of 320 F/g at a 0.33 A/g discharge current density. Thirty thousand charge–discharge (CD) cycles at a heavy CD current density of 3.3 A/g were carried out on the supercapacitor cell. The values of equivalent series resistance (ESR) (8–9 Ω) and efficiency (100–98%) were found to be independent of the cycle number with an excellent retention capacity of 83%. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41711.

INTRODUCTION

Supercapacitors have been of great interest because of their high power densities (Ps), large cycle life, and lack of toxic materials.[1,2] The capacitance performance of supercapacitors depends on active electrode materials based on carbon materials, metal oxides, and conducting polymers, which have their own advantages and disadvantages. Supercapacitors can be classified into two major types based on electrode materials, that is, electrochemical double-layer capacitors consist of carbon materials and pseudocapacitors based on metal oxide or conducting polymers. Among the metal oxides, hydrous ruthenium oxide is recognized as one of the most promising candidates for electrode materials with its good capacitance and rate capability, but its use in supercapacitors is discouraged because of its low abundance, high cost, and toxicity. In addition to the performance and cost considerations of transition-metal oxides, there is a steadily increasing awareness of safety risks and environmental problems inherent in the various technologies. Research and development on conducting polymer-based materials in supercapacitor applications have received a great deal of interest in the recent years because of their low cost, easy synthesis, controllable electrical conductivity, fast doping/dedoping process, and good environmental stability.[3]

To select a low-cost material with electrode stability, in this study, we selected polyaniline from the conducting polymer group and titanium dioxide (TiO_2) from the metal oxide group. The thermally stable, nonflammable, poorly soluble, and naturally available metal oxide, TiO_2, is a global product with many important applications; it has been proven as safe in its intended use over many decades. Moreover, TiO_2 is preferred in the preparation of hybrid materials with PANI because the conduction band of TiO_2 matches well with the lowest unoccupied molecular orbital of PANI and possibly enhances the electronic transport properties.[4,5]

PANI has a poorer electrochemical stability than TiO_2, and the performance of PANI can be improved with TiO_2 because of the donor–acceptor interactions between PANI and the metal oxide surface.[6] TiO_2 is one of the typical *n*-type materials, whereas polyaniline is a *p*-type material.

Few reports are available in the literature concerning the synthesis of PANI–TiO_2[7] and its use in supercapacitors.[8,9] A highly homogeneous hybrid PANI–TiO_2 was synthesized by the chemical oxidation polymerization of aniline with the simultaneous hydrolysis of $Ti(SO_4)_2$ with ammonium persulfate by Li et al.[8] PANI–TiO_2 was synthesized via the *in situ* polymerization of

aniline in the presence of nano-TiO_2 and used in a supercapacitor by Aishui et al.[9] However, in both of the previous studies, the electrochemical performance of PANI–TiO_2 was carried out with three electrode configurations. Recently, we reported the use of PANI–TiO_2 hybrid materials in supercapacitor applications via the in situ synthesis of aniline to polyaniline salt in the presence of TiO_2.[10]

In this study, peroxotitanium acid (PTiA) was used to oxidize aniline in the presence of sulfuric acid to a poly(aniline sulfate) salt–titanium oxide composite in one step. This composite was characterized by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDAX) analyses. This composite was used as an electrode in a supercapacitor, and its electrochemical performance was estimated through cyclic voltammetry (CV) and impedance analyses.

EXPERIMENTAL

Materials and Measurements

Sulfuric acid, titanium tetrachloride, and ammonia (25%) and hydrogen peroxide (30%) solutions were purchased from S. D. Fine Chemicals (Mumbai, India) and used as supplied. Graphite powder (<20 μm) was purchased from Sigma Aldrich. Graphite foil (0.013 mm thickness) supplied by Alfa Aesar (India) was used for the current collector.

The FTIR spectra of the powder samples were registered on a gas chromatograph–FTIR spectrometer 670 Nicolet Nexus (Minnesota) with the KBr pellet technique. XRD profiles for the powders were obtained on a Bruker AXS D8 Advance X-ray diffractometer (Karlsruhe, Germany) with Cu Kα radiation (land continuous; $\lambda = 1.54$ Å) at a scan speed of 0.045°/min. We used the powder samples by employing a standard sample holder. Morphological study and EDAX were performed with a Hitachi S3400 scanning electron microscope (Tokyo, Japan). The powder sample was mounted on a double-sided adhesive carbon disk and sputter-coated with a thin layer of gold (500 Å) to prevent the sample from possibly charging. Thermogravimetric analysis was performed on a TA Instruments Q500 thermogravimetric analyzer (New Castle, DE) for PANI–TiO_2 powders at a heating rate of 10°C/min from ambient temperature to 700°C under a nitrogen atmosphere.

Electrode Preparation

An amount of 36 mg of PANI–TiO_2 and 14 mg of graphite were ground for 30 min, and 3 mg of this mixed sample was pressed on graphite foil at 100 kg/cm^2. A supercapacitor cell (Swagelok-type cell) was constructed with two PANI–TiO_2 electrodes in a $1M$ aqueous H_2SO_4 electrolyte solution without a reference electrode. CV and galvanostatic charge–discharge (CD) experiments were carried on supercapacitor cell with a WonA-Tech. multichannel potentiostat/galvanostat instrument (WMPG1000, Gyeonggi-Do, Korea). Cyclic voltammograms were recorded from 0 to 0.6 V at various sweep rates. Galvanostatic CD experiments were carried out from 0 to 0.6 V at various current densities. Electrochemical impedance spectroscopy (EIS) measurements were carried out with an IM6ex zahner-Elektrik instrument (Germany) in the frequency range 40 kHz
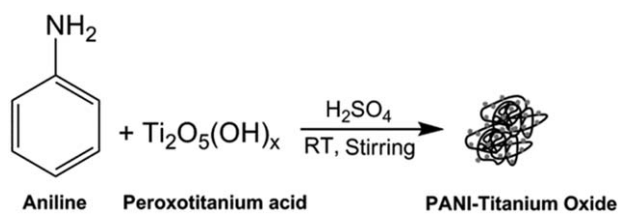
Scheme 1. Schematic representation of the PANI–TiO_2 synthesis.

to 10 mHz at various voltages with a three-electrode configuration, that is, with polyaniline salt as a working electrode, a platinum counter electrode, a saturated calomel electrode as a reference electrode, and a $1M$ aqueous H_2SO_4 electrolyte solution. All of the electrochemical measurements were performed at ambient temperature.

Preparation of PTiA

PTiA was prepared according to a previous report.[11] Briefly, ethanol (5 mL) and distilled water (200 mL) were placed in a 500-mL beaker. We kept the beaker in an ice bath and cooled it to 2–3°C. A volume of 5 mL of $TiCl_4$ was added slowly to the previous solution and stirred for 30 min. We adjusted the pH of the solution to 8–9 by adding the required amount of 25% ammonia solution. The formed white precipitated was filtered and washed with an ample amount of distilled water to eliminate the unreacted reactants and impurities. The white precipitate was transferred into a beaker containing 100 mL of distilled water. The hydrogen peroxide (30 wt %) solution was added dropwise into the previous mixture under cold conditions until the pH of the solution became 4–5. We evaporated water at ambient temperature by keeping the mixture for approximately 2 days; this gave them a yellow colored gel.

Synthesis of PANI–TiO_2

An amount of 20 g of yellow colored gel containing PTiA was added to 30 mL of a $1M$ aqueous sulfuric acid solution placed in a 100-mL beaker, and then, we stirred the mixture for 15 min. A volume of 1 mL of aniline was added directly to the previous solution and stirred for 8 h at ambient temperature. The green precipitate was filtered, washed with an ample amount of water and, finally, with 250 mL of acetone. The powder sample was dried at 50°C in an oven until it reached a constant weight.

Calcination

PANI–TiO_2 (500 mg) was heated up to 800°C in a furnace under atmospheric conditions, and the sample weight was found to be 250 mg. Because at 800°C all of the PANI samples escaped, the remaining sample indicated the weight of TiO_2. The PANI–TiO_2 composite contained an equal amount of PANI and TiO_2.

RESULTS AND DISCUSSION

Aniline was oxidized with PTiA in the presence of sulfuric acid to the poly(aniline sulfate) salt composite with TiO_2 (Scheme 1), wherein PTiA acted as an oxidizing agent and a source of TiO_2. We carried out the polymerization by varying the amount of aniline monomer and also the reaction time. The values of the yield

Table I. Yield and Conductivity Values for Polyaniline Salts with Various Amounts of Aniline Used in the Reaction

Aniline (mL)	Yield (g)	Conductivity (S/cm)
0.2	0.50	2.3×10^{-3}
0.3	0.60	2.8×10^{-3}
0.4	0.70	2.8×10^{-3}
0.5	0.74	3.0×10^{-3}
0.6	0.78	3.2×10^{-3}
0.7	0.84	5.2×10^{-3}
0.8	0.94	5.7×10^{-3}
0.9	1.12	7.1×10^{-3}
1.0	1.06	8.1×10^{-3}

and conductivity of the polyaniline–titanium oxide composites are reported in Table I.

First, the amount of aniline increased from 0.2 to 1 mL in steps of 0.1 mL. The values of the yield and conductivity increased with increasing amount of aniline, and a maximum value was attained at 1 mL of aniline. Subsequently, the yield and conductivity were determined within 24 h, and the values of the yield and conductivity attained a maximum at 8 h (Table II).

The optimization of the reaction conditions for the preparation of the polyaniline–titanium oxide composite was obtained on the basis of the yield and conductivity values, that is, the use of PTiA gel (20 g), sulfuric acid (1M), aniline (1 mL), total volume (100 mL), reaction time (8 h), and temperature (ambient temperature). The sample prepared with the optimized reaction condition is represented as PANI–TiO$_2$ in this article, and it was subjected to further analyses.

FTIR Study
The FTIR spectrum of PTiA is shown in Figure 1(a). This spectrum showed broad peaks at 3200 to 3400 cm^{-1} that were due to the hydroxyl groups of the water molecules. A peak at 1620 cm^{-1} represented the bending vibrations of the water molecule. The peak at 905 cm^{-1} was attributed to the peroxo group.[11] The peak at 1400 cm^{-1} was attributed to the N—H bond, which indicated the presence of NH$_4^+$.[12] The FTIR spectrum of TiO$_2$ showed that the broad band centered at 520 cm^{-1} was likely due to the vibration of the Ti—O bond in

**Table II.** Yield and Conductivity Values for Polyaniline Salts with the Reaction Time

Reaction time (h)	Yield (g)	Conductivity (S/cm)
1	0.82	6.9×10^{-3}
2	0.97	7.2×10^{-3}
3	1.01	7.2×10^{-3}
4	1.03	7.4×10^{-3}
6	1.05	7.6×10^{-3}
8	1.06	8.1×10^{-3}
10	1.10	8.1×10^{-3}
20	1.15	8.1×10^{-3}
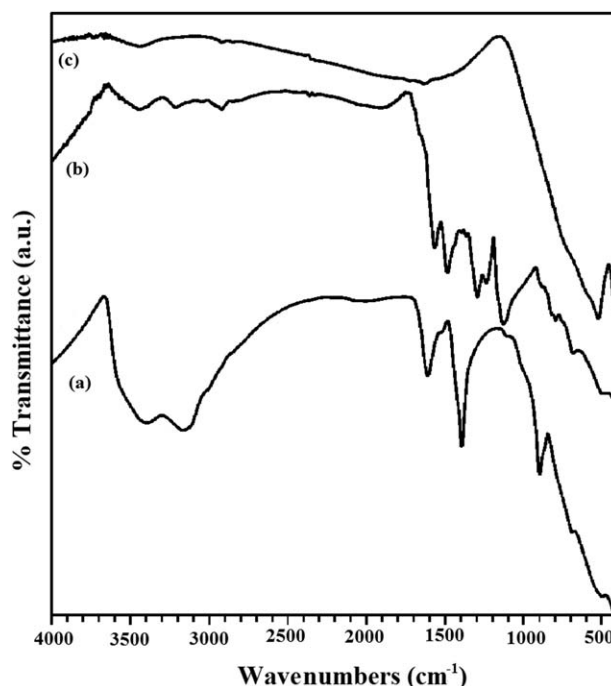
Figure 1. FTIR spectra of (a) PTiA, (b) PANI–TiO$_2$, and (c) calcined PANI–TiO$_2$.

the TiO$_2$ lattice.[13] Two broad peaks observed at 1640 and 3445 cm^{-1} were assigned to the vibrations of the hydroxyl groups.[14] The FTIR spectrum of PANI–TiO$_2$ is shown in Figure 1(b), and the peak positions were due to the normal polyaniline salt. The peaks due to TiO$_2$ were not seen. This result indicates that TiO$_2$ was covered by PANI. Figure 1(c) represents the spectrum of the rutile form of TiO$_2$;[15] this was obtained from the calcination of PANI–TiO$_2$ material.

XRD Study
The XRD pattern of PTiA is shown in Figure 2(a), and it shows a peak at $2\theta = 8.5$. The XRD pattern of PANI–TiO$_2$ [Figure
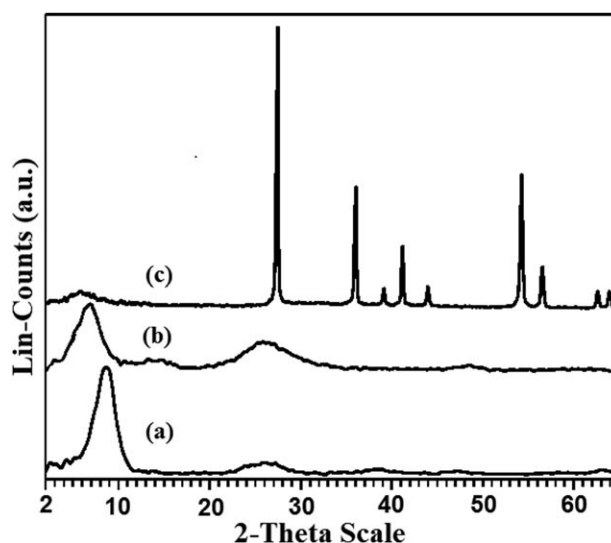
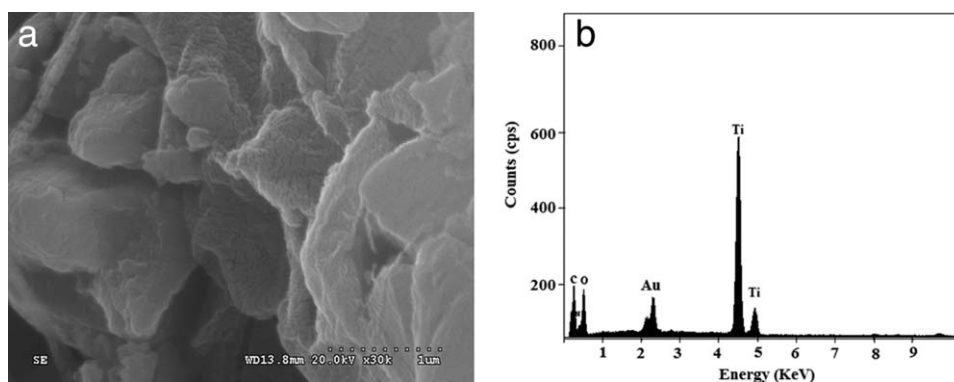**Figure 2.** XRD spectra of (a) PTiA, (b) PANI–TiO$_2$, and (c) calcined PANI–TiO$_2$.

Figure 3. (a) SEM image of PANI–TiO$_2$ and (b) EDAX spectrum of PANI–TiO$_2$.

2(b)] showed a broad peak around $2\theta = 25$, which was due to amorphous PANI and another broad peak at $2\theta = 7$, which was due to the oxide of titanium. The XRD patterns of calcinated PANI–TiO$_2$ at 800°C showed peaks at $2\theta = 27.4$, 36.1, 39.1, 41.2, 44.0, 54.3, 56.6, 62.7, and 64 [Figure 2(c)], which designated the rutile phase of TiO$_2$ and was authenticated from JCPDF number 860147.

Morphology Study

The field emission SEM results of PANI–TiO$_2$ are shown in Figure 3(a). The SEM image showed a flakelike morphology, which befitted ion diffusion and migration in the composite. The corresponding EDAX spectrum is presented in Figure 3(b). EDAX of PANI–TiO$_2$ showed the presence of carbon, oxygen, and titanium elements. This result supported the presence of titanium in the composite.

TGA Study

We carried out the thermal stability of the PANI–TiO$_2$ material by recording TGA, as shown in Figure 4. TGA of PANI–TiO$_2$ showed an initial weight loss step of 9 wt % up to 105°C; this indicated the presence of water molecules. On further heating, it showed a weight loss step (3.5 wt %) up to 270°C, which was due to the elimination of water in adduct form, the solvent, and so on.On further heating, it showed another weight loss step (3.5 wt %) up to 340°C; this was due to the degradation of
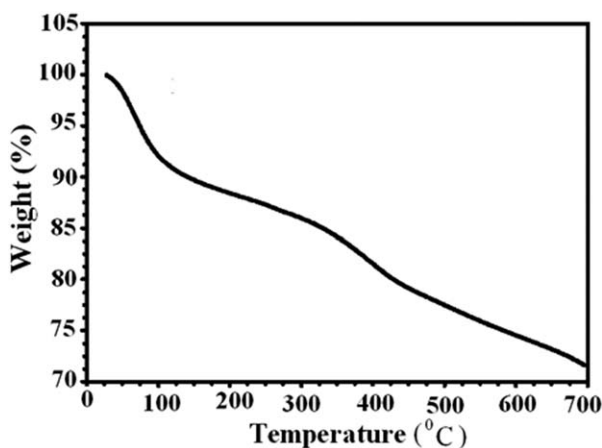
low-molecular-weight oligomer, trapped solvents, and so on. The polymer could be considered stable up to 300°C.

Studies of the electrochemical performances of the polyaniline metal oxide in a symmetric supercapacitor configuration have been carried out in recent years.[16–19] Here, we discuss the PANI–TiO$_2$ symmetric supercapacitor results.

CV Study

The cyclic voltammogram of the PANI–TiO$_2$ cell was scanned in the potential range 0–0.6 V from lower to higher scan rates (Figure 5). First, the absence of redox peaks indicated that the supercapacitor was charged and discharged at a pseudo-constant rate over the whole voltammetric cycle. Second, we observed a square voltammetric response with marginal IR effects at low scan rates up to 10 mV/s; this indicated that the composite film exhibited a high intrinsic electrical conductivity and good kinetic reversibility. These were important factors for capacitor behavior. A similar result was reported for polyaniline–manganous dioxide symmetric supercapacitor cell by Cheng *et al.*[20] Another observation is that even with a very high scan rate at 100 mV/s, the shape of the CV curve was still maintained, and this demonstrated the high performance of the supercapacitor.[21] The capacitance value (C) for the symmetric capacitor was calculated from the cyclic voltammogram with the following formula:
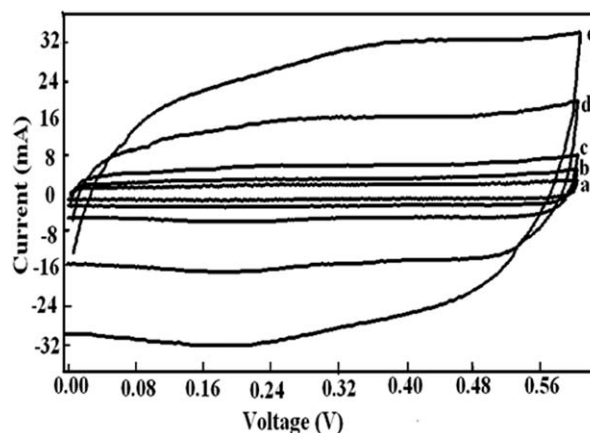

Figure 4. TG thermogram of PANI–TiO$_2$.

Figure 5. Cyclic voltammograms of PANI–TiO$_2$ in $1M$ H$_2$SO$_4$ electrolyte at various sweep rates: (a) 5, (b) 10, (c) 20, (d) 50, and (e) 100 mV/s.
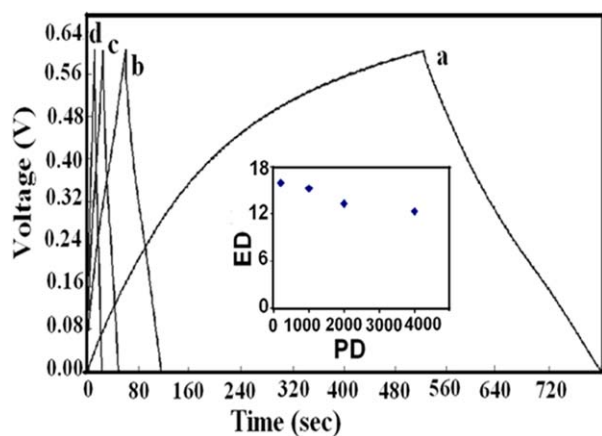
Figure 6. Galvanostatic CD curves of PANI–TiO$_2$ at current densities of (a) 0.33, (b) 1.66, (c) 3.3, and (d) 6.6 A/g. ED, energy density; PD, power density. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$C = 2i_{Avg}/ms$$

where s is the potential sweep rate, m is the mass of the electrode, and i_{Avg} is the average current. The specific capacitance values calculated from the CV tests (CV-C_s) were 330, 300, 250, 210, and 200 F/g at scan rates of 5, 10, 20, 50, and 100 mV/s, respectively (Figure 5). At slower scan rates, the diffusion of ions from the electrolyte could gain access to almost all available materials of the

electrode; this led to an effective insertion and de-insertion processes. However, when the scan rate increased, the effective interaction between the ions and electrode was greatly reduced, and the redox reaction was limited only to the outer surface of the electrode. Hence, there was a reduction in the capacitance.[22,23]

CD Study

Galvanstatic CD studies of the PANI–TiO$_2$ cell was carried out in the potential range 0–0.6 V at various dicharge current densities (Figure 6). The discharge-specific capacitance (C_d), energy density (E), and power density (P) were calculated from the following formula:

$$C_d = I \times 2\Delta t/\Delta V \times m$$

$$E = \Delta V \times I \times \Delta t/3600 \times m$$

$$P = \Delta V \times I/m$$

here I is the charge–discharge current, Δt is the discharge time, ΔV is the voltage difference, and m is the mass of active material within the electrode. The capacitance values (CD-C_s) are 320, 275, 266, and 244 F/g with discharge curent densities of 0.33, 1.66, 3.3, and 6.6 A/g, respectively.

The Ragone plot of energy versus P is depicted as an inset in Figure 6. The capacitance retention over prolonged CD cycles was essential for practical supercapacitor materials. Hence, CD experiments were carried out for a PANI–TiO$_2$ cell at a high current density (3.3 A/g) for 30,000 cycles. The CD curves for the first 10 and last 10 cycles are shown in Figure 7(a,b).
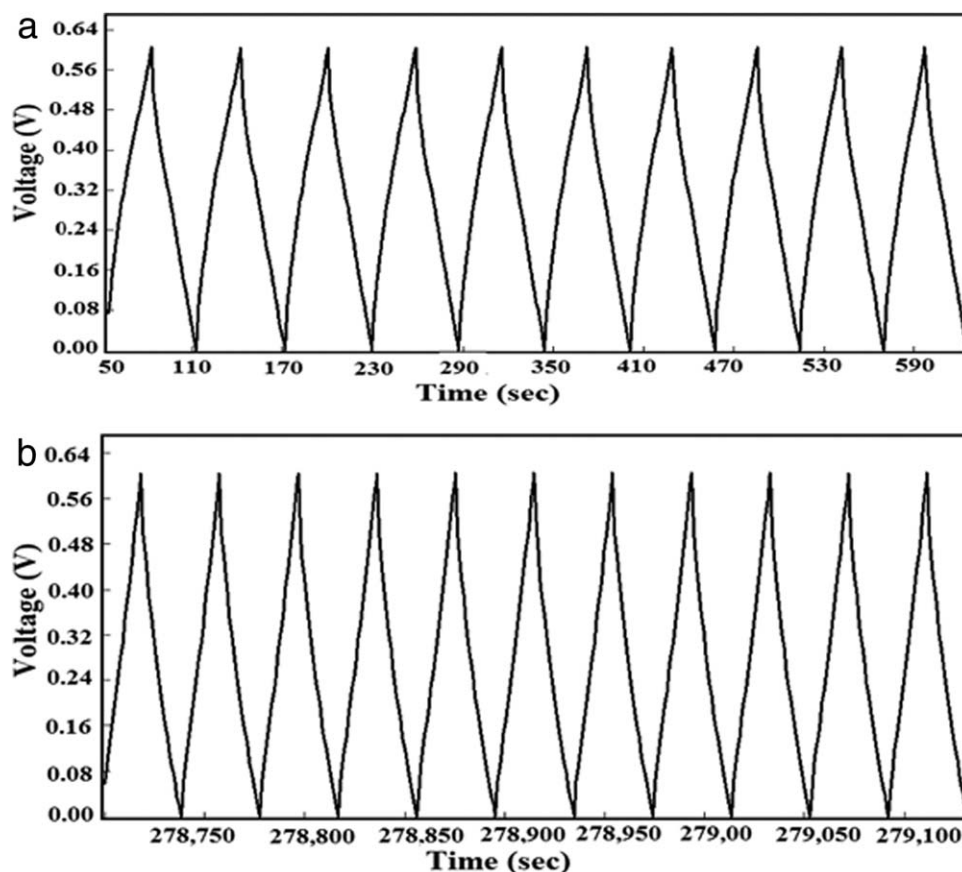

Figure 7. (a) First and (b) last 10 cycles of 30,000 cycles at a current density of 3.3 A/g.
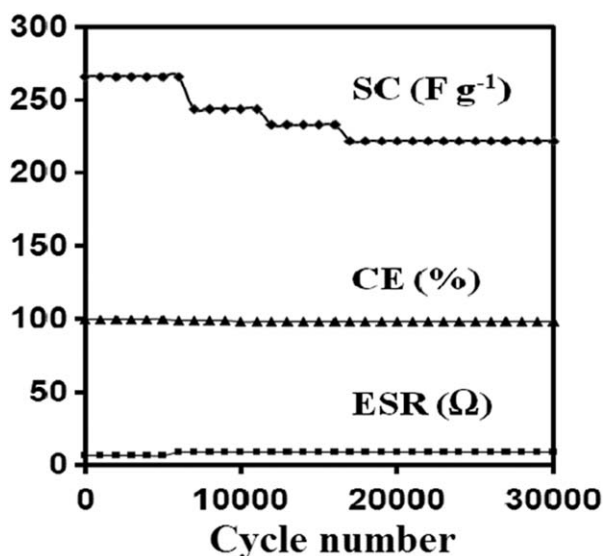
Figure 8. Cycle stability of a PANI–TiO$_2$ cell for 30,000 cycles at a current density of 3.3 A/g.

The value of CD-C_s after 30,000 cycles was found to be 220 F/g; that is, there was an 83% retention of capacitance. Moreover, the values of the coulombic efficiency (100–98%) and equivalent series resistance (ESR) (8 to 9) were found to be independent of the cycle numbers (Figure 8). The values of the specific

capacitance (CD-C_s), energy density (E), and power density (P) with respect to the weight of one electrode were 265 F/g, 13 W h/kg, and 2000 W/kg, respectively. This result was due to the formation of a well-ordered conducting PANI/nano-TiO$_2$ composite; this allowed for better accommodation of the volume changes during CD without the initiation of the fracture that may occur in bulk or micrometer-sized materials.[24]

The CD results of the PANI–TiO$_2$ system reported in the literature are given in Table III. Li et al.[8] and Aishui et al.[9] studied the CD behavior of the PANI–TiO$_2$ electrode system (a three-electrode configuration). In our group, we recently studied the CD behavior of a PANI–TiO$_2$ cell system, wherein PANI–TiO$_2$ was prepared by the *in situ* polymerization of aniline in the presence of TiO$_2$. This showed a capacitance value of 205 F/g at 2 A/g with a capacitance retention of 65% after 1700 cycles. In this study, we carried out CD behavior at a higher current density of 3.3 A/g for even 30,000 cycles. This showed a much better performance; that is, a higher capacitance value of 266 F/g, even at a current density of 3.3 A/g, with a higher capacitance retention of 83% after 30,000 cycles (Table III).

EIS

EIS was further used to study the frequency behavior of the supercapacitor. It provided information regarding the capacitance behavior, phase angle with respect to frequencies, and also solution resistance. The PANI–TiO$_2$ electrode was subjected to

Table III. Comparison of CD Results Reported in the Literature

| Aqueous polymerization pathway	Electrode	Capacitance at CD current density	Number of cycles/ capacity retention	Reference
Aniline + Ti(SO$_4$)$_2$ + (NH4)$_2$S$_2$O$_8$	Single electrode: PANI-TiO$_2$	495 F/g at 2.5 A/g	3000/50%	8
Aniline + HCl + TiO$_2$ + (NH4)$_2$S$_2$O$_8$	Single electrode: PANI-TiO$_2$	330 F/g at 1.5 A/g	10,000/92%	9
Aniline + H$_2$SO$_4$ + TiO$_2$ + (NH4)$_2$S$_2$O$_8$	Cell system: PANI-TiO$_2$/PANI-TiO$_2$	205 F/g at 2 A/g	1700/65%	10
Aniline + H$_2$SO$_4$ + Ti$_2$O$_5$(OH)$_x$	Cell system: PANI-TiO$_2$/PANI-TiO$_2$	266 F/g at 3.3 A/g	30,000/83%	This study
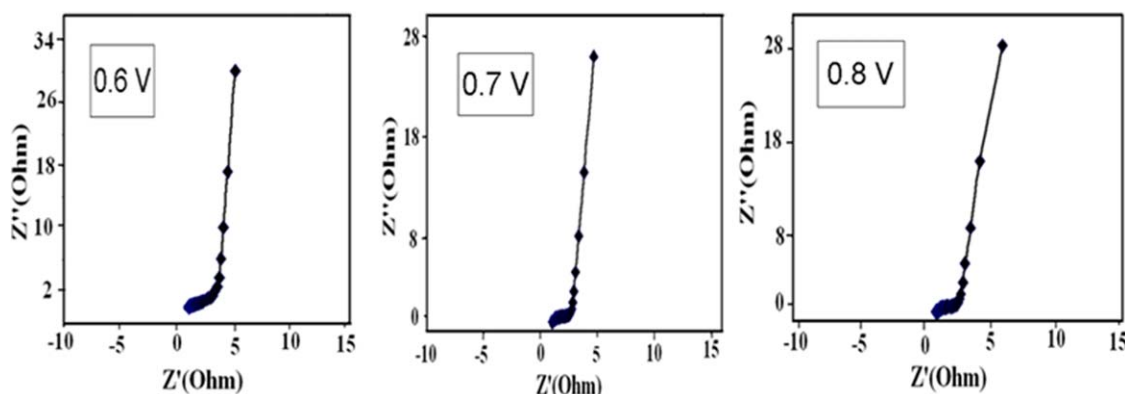
Figure 9. Nyquist plots of PANI–TiO$_2$ at 0.6, 0.7, and 0.8 V in 1M H$_2$SO$_4$. Z′, real impedance; Z, imaginary impedance. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
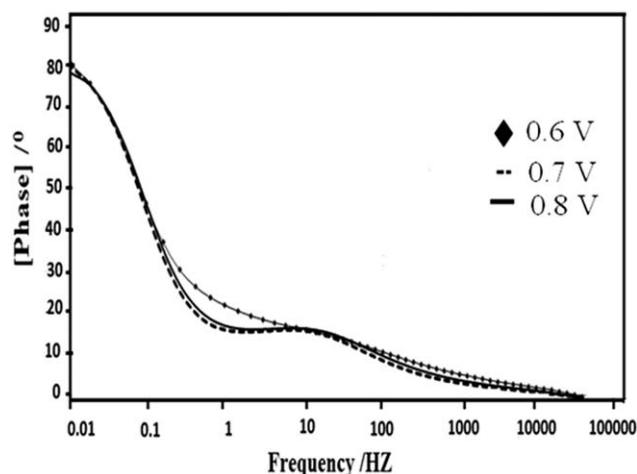
Figure 10. Bode plots of PANI–TiO₂ at 0.6, 0.7, and 0.8 V in $1M$ H₂SO₄.

various applied potentials (0.6, 0.7, and 0.8 V) in a $1M$ aqueous solution of an H₂SO₄ electrolyte, and the impedance characteristics were recorded (Figure 9). The corresponding bode plots are shown in Figure 10. As shown, a semicircle appeared in the high-frequency region; this showed resistance during charge transfer at the electrode/electrolyte interface. The linear part at lower frequencies originated from the diffusive resistance from the bulk solution to the electrode surface and also within the electrode pores. From the Nyquist plot, the bulk solution resistance was calculated, and it provided almost the same (0.92–1.0 Ω) with the applied voltages. The value of the specific capacitance was calculated from the following formula:

$$C = -1/(2\Pi f z_{im} m)$$

where $\pi = 3.14$, f is the frequency, Z_{im} is the imaginary impedance at f, and m is the mass of the material. The capacitance values for the PANI–TiO₂ electrode at 10 mHz were 185, 210, and 195 F/g with voltages of 0.6, 0.7, and 0.8 V, respectively. The phase angles for PANI–TiO₂ from the bode plot were 80.3, 79.8, and 78.1 at 0.6, 0.7 and 0.8 V, respectively (Figure 10).

CONCLUSIONS

A PANI–TiO₂ composite was successfully synthesized directly by the oxidation of aniline with PTiA. Thirty thousand CD cycles at a heavy CD current density of 3.3 A/g were carried out on the supercapacitor cell. The values of the ESR and efficiency were found to be independent of the cycle number. They showed an excellent retention capacity value of 83.5%. This composite material could be a suitable material for the supercapacitor application.

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