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Hybrid Material of PANI with TiO₂-SnO₂: Pseudocapacitor Electrode for Higher Performance SupercapacitorsRavi Bolagam,^[a, c] Rajender Boddula,^[a] and Palaniappan Srinivasan^{*[a, b, c]}

Mixed metal oxide composites of TiO₂-SnO₂ were prepared by varying the quantities of SnCl₂·2H₂O by the impregnation method to TiO₂. Aniline monomer was polymerized in the suspension of TiO₂-SnO₂ to form organic-inorganic composite materials, in which metal oxide particles were embedded within polyaniline (PANI-SA). Formation of the composite was confirmed from FT-IR, XRD and EDAX analyses and morphological image was found from FE-SEM. The electrochemical properties were investigated using CV, CD and EIS analyses. PANI-SA•TiO₂-SnO₂ showed higher electrochemical perform-

ances than that of PANI-SA•TiO₂ or PANI-SA•SnO₂, which are attributed from (i) higher electron transfer rate due to reduction in band gap and (ii) more space between the nano rods, which allow the electrolyte to interact more surface of the electrode. The best PANI-SA•TiO₂-SnO₂ material exhibited a specific capacitance of 540 F g⁻¹ with an energy density of 27 Wh kg⁻¹ at a power density of 200 W kg⁻¹. Retention in capacitance of 85% was obtained even at 6000 cycles and this organic-inorganic composite fulfilled the requirement of long durability necessary for an energy storage system.

Introduction

The design and synthesis of high power and long life span supercapacitors (SCs) are urgently needed to meet the increasing requirement in the field of portable devices, electrical/hybrid electric vehicles.^[1,2] Among the many investigated electrode materials, conducting polymers and metal oxides are considered to be good alternatives due to their high capacitance from pseudocapacitance. In the category of conducting polymers, polyaniline (PANI) is considered as a most promising material because of its high capacitive characteristic, low cost, facile synthesis and environmental stability.^[3,4] However, the poor stability during the charge-discharge process restricts its practical application in a supercapacitor. One of the ways to improve the performance of PANI based supercapacitors regarding stability is to combine PANI with metal oxide materials.^[5-7] Use of metal oxides such as RuO₂,^[8] MnO₂,^[9] V₂O₅,^[10] SnO₂,^[11] TiO₂^[5] with polymer contribute pseudocapacitance as well as enhance the stability of composite materials. Among these metal oxides materials, TiO₂/SnO₂ are excellent candidates for electrode materials due to their low

cost, eco-friendliness and particularly negligible volume expansion during the discharge-charge process, which lead to long cycle life and durability.^[11-14] Moreover, TiO₂/SnO₂ is preferred in the preparation of hybrid materials with PANI because the conduction band of TiO₂/SnO₂ matches well with the lowest unoccupied molecular orbital of PANI and possibly enhances the electronic transport properties.^[15,16] Electrochemical performances of PANI-TiO₂ have been carried out in the literature via three electrodes configuration, and the results are given in Table 1. However, for practical application, it should be carried out in two electrodes configuration. Recently, we reported in two electrodes configuration, and PANI-TiO₂ system showed a specific capacitance value of 355 F g⁻¹ with energy and power density of 17.7 Wh kg⁻¹ and 200 W kg⁻¹ respectively.^[17] Similarly, many reports are available regarding the electrochemical performances of PANI-SnO₂ in the literature, which are again in three electrodes configuration (Table 1).

By considering the excellent cycling stability and high capacitance of SnO₂, the good stability of TiO₂ and the superior match in the lattice level of the two semiconductors with polyaniline conduction band, in this work, we prepared the composite of PANI-SA•TiO₂-SnO₂ as electrode materials for high-performance supercapacitors. PANI-SA•TiO₂-SnO₂ samples have been characterized by FT-IR, XRD and FE-SEM. These samples have been used as electrode in symmetric cell configuration and evaluated their electrochemical performances.

Results and discussion

The aim of this work is to find out the performances of polyaniline composites of mixed metal oxide in supercapacitor application. Initially, various composition of mixed metal oxide of TiO₂ and SnO₂ were prepared by varying the quantity of starting metal oxide (TiO₂) and metal oxide precursor (SnCl₂·2H₂O).

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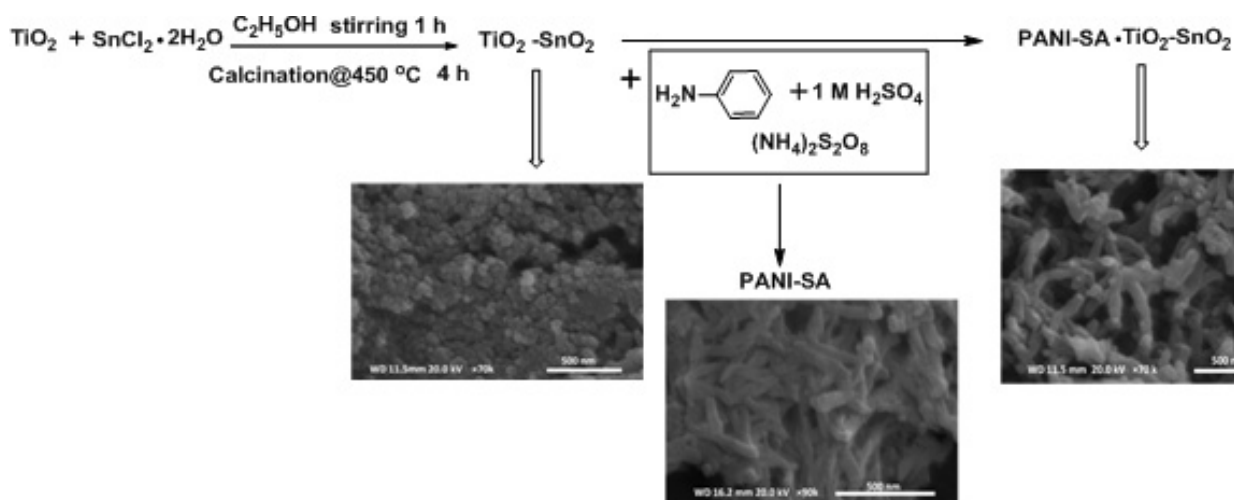
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Table 1. Literature survey of PANI•TiO₂ and PANI•SnO₂ composite electrodes in supercapacitor application

Ref no.	C _s (F g ⁻¹)	CV/ CD	E _d (Wh Kg ⁻¹)	P _d (W Kg ⁻¹)	Cycle life @ current density	Configuration	Voltage (V)	Electrolyte
PANI-TiO ₂								
[18]	422	CD	76	756	500 7 A g ⁻¹	3 electrode	0 to 0.6	1 M HCl
[7]	783	CV	–	–	5000	3 electrode	-0.2 to 0.8	1 M H ₂ SO ₄
[19]	380	CD	38	300	1000 5 A g ⁻¹	3 electrode	0 to 0.6	1 M HCl
[20]	800	CV	–	–	–	3 electrode	-0.5 to 1	0.5 M H ₂ SO ₄
[21]	442	CD	–	–	–	3 electrode	-0.2 to 0.8	1 M H ₂ SO ₄
[22]	497	CD	49	420	1000 7 A g ⁻¹	3 electrode	0 to 0.6	1 M HCl
[23]	784	CV	–	–	–	3 electrode	-0.2 to 0.8	0.5 M H ₂ SO ₄
[24]	740	CD	–	–	1100 3 A g ⁻¹	3 electrode	0 to 1	1 M H ₂ SO ₄
[25]	330	CD	–	–	10000 1.5 A g ⁻¹	3 electrode	0.05 to 0.55	1 M H ₂ SO ₄
[17]	355	CD	17.7	200	1700 2 A g ⁻¹	2 electrode	0 to 0.6	1 M H ₂ SO ₄
PANI-SnO ₂								
[26]	305	CD	42.4	666	500	3 electrode	-0.2 to 0.8	1 M H ₂ SO ₄
[27]	219	CD	–	–	–	3 electrode	0 to 0.75	1 M HClO ₄
[28]	721	CV	–	–	1600	3 electrode	0 to 0.8	1 M H ₂ SO ₄
[1]	335	CD	–	–	10000 15 A g ⁻¹	3 electrode	0 to 1.0	1 M H ₂ SO ₄
[29]	173	CV	–	–	–	3 electrode	-0.2 to 0.8	1 M H ₂ SO ₄
[30]	501	CD	67	960	20000.5 A g ⁻¹	2 electrode	-0.5 to 0.5	1 M H ₂ SO ₄



Scheme 1. Preparation of TiO₂-SnO₂ and its composites with polyaniline salt (PANI-SA•TiO₂-SnO₂).

O), then, polyaniline salt containing mixed metal oxides were prepared by the chemical oxidative polymerization of aniline using ammonium persulfate in presence of sulphuric acid and mixed metal oxides (Scheme 1). These polyaniline containing mixed metal oxides were characterized by FT-IR, XRD, SEM, EDAX and electrochemical studies and the results are discussed here.

FTIR spectra of hybrids

The FT-IR spectra of PANI, TiO₂-SnO₂(10%) and their composites are shown in Figure 1. FT-IR spectrum of TiO₂-SnO₂(10%) is not showing any clear peak (Figure 1a) except a broad peak around 3400 indicates the presence of moisture. FT-IR spectrum of PANI-SA is shown in Figure 1e, which shows characteristic peaks of polyaniline, such as 3445 cm⁻¹ (N-H str.), 2917 cm⁻¹ is due to (aromatic C-H stretching vibrations), 1565 (C=C str., quinonoid ring), 1477 cm⁻¹ (C=C str., benzenoid ring),

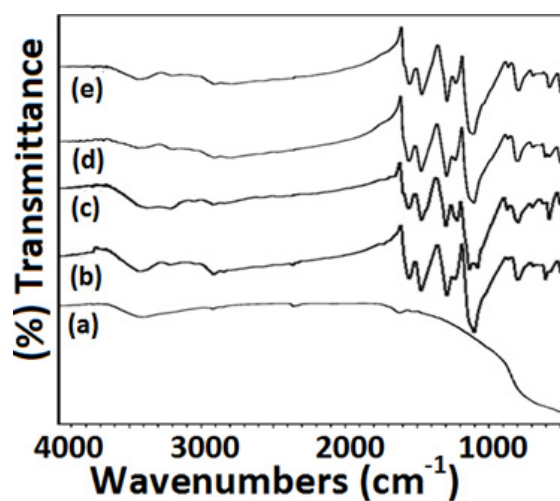


Figure 1. FTIR spectra of (a) TiO₂-SnO₂(10%) (b) PANI-SA•SnO₂, (c) PANI-SA•TiO₂, (d) PANI-SA•TiO₂-SnO₂(10%), (e) PANI-SA.

1303 cm^{-1} (C–N str., quinonoid ring), 1240 cm^{-1} (C–N str., benzenoid ring), 1110 cm^{-1} (N=Q=N vibration, where Q represents the quinonoid ring), 802 cm^{-1} (1,4-disubstituted benzene) and 507 (C–H out-of-plane bending vibration). The FT-IR spectra of PANI-SA•SnO₂ (Figure 1b) PANI-SA•TiO₂ (Figure 1c), PANI-SA•TiO₂-SnO₂ (Figure 1d) are very similar to that of the FT-IR spectrum of PANI-SA, except a slight shift in the absorption peaks, due to changes in the electron density in the quinonoid ring of the polyaniline salt.^[25,31]

Diffraction patterns of hybrid

Synthesized materials were confirmed from XRD spectra (Figure 4). XRD spectrum of the composite TiO₂-SnO₂(10%) showed

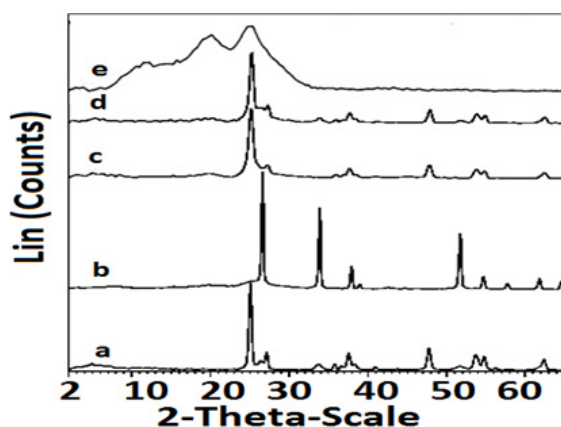


Figure 2. XRD patterns of (a) TiO₂-SnO₂(10%), (b) PANI-SA•SnO₂, (c) PANI-SA•TiO₂, (d) PANI-SA•TiO₂-SnO₂(10%) and (e) PANI-SA.

many peaks. The diffraction peaks at 26.6, 33.8, 37.6, 51.7, 54.8, 62.4 confirm the presence of SnO₂ [32](JCPDS card no. 41–1445), peaks at 37.5, 47.8, 53.8 are due to anatase TiO₂ (JCPDS 21–1272), and the peaks 27.2, 35.8, 54.8 are due to rutile TiO₂ [33] (JCPDS 21–1276)(Figure 2a). The composite of TiO₂-SnO₂ consists of anatase and rutile TiO₂ forms and SnO₂. XRD spectrum of PANI-SA showed peaks at 10°, 20° and 25° corresponding to polyaniline salt [34](Figure 2e). XRD spectra of PANI-SA•SnO₂ (Figure 2b) PANI-SA•TiO₂ (Figure 2c) and PANI-SA•TiO₂-SnO₂(10%) (Figure 2d) showed the presence of both polyaniline and corresponding metal oxide.

Morphology of polyaniline–metal oxide composites

Morphological behaviour of PANI-SA and its metal oxide composites were carried by FE-SEM analyses and the images are shown in Figure 3. For better comparison, SEM images recorded in the length of 500 nm are shown in Figure 3a to 3g and for clarity, SEM images recorded at higher magnitude of 200 nm length for the three samples are given in Figure 3h to 3j. SEM image of mixed metal oxide, TiO₂-SnO₂(10%), showed uniform spherical morphology of diameter 20 to 35 nm size (Figure 3a), whereas, PANI-SA showed (Figure 3b) uniform nano

rods of width (40 to 50 nm) and length (150 to 300 nm). SEM images of polyaniline salt composites with metal oxides showed nano rods morphology (Figure 3c to 3g), which is similar to that of the morphology of polyaniline salt. Nano rods are not clear in Figure 3c, 3d and these are visible in higher magnitude images (Figure 3i and 3j). This result signposts that the preparation of polyaniline metal oxide composite via in-situ polymerization of aniline in presence of metal oxide results in nano rods morphology, indicating that metal oxide is covered by polyaniline. Size of the nano rods for polyaniline and its metal oxide composites are PANI-SA [Width=40 – 50 nm and Length=150 – 300 nm], PANI-SA•SnO₂ [less than PANI-SA], PANI-SA•TiO₂ [W=50 – 100 nm and L=450 – 550 nm], PANI-SA•TiO₂-SnO₂(5%) [W=50 – 80 nm and L=200 – 300 nm], PANI-SA•TiO₂-SnO₂(10%) [W=50 – 60 nm and L=150 – 300 nm], and PANI-SA•TiO₂-SnO₂ (15%) [W=45 – 50 nm and L=340 – 400 nm]. An observation is that the space between the nano rods increases in the following order PANI-SA•TiO₂-SnO₂ (10%) \cong PANI-SA•TiO₂-SnO₂(15%) > PANI-SA•TiO₂-SnO₂(5%) > PANI-SA > PANI-SA•TiO₂ > PANI-SA•SnO₂.

EDAX spectra

Formation of metal oxide composite and its composite with polyaniline salt was found from EDAX spectra. EDAX spectra of TiO₂-SnO₂(10%) and its composite with polyaniline salt are shown in Figure 4. EDAX of TiO₂-SnO₂(10%) composite shows the presence of elements such as Sn and Ti (Figure 4a) indicates the presence of TiO₂ and SnO₂ in the composite of TiO₂-SnO₂ (10%). EDAX spectrum PANI-SA•TiO₂-SnO₂(10%) (Figure 4b) shows the elements such as S, Ti and Sn, which signposts the presence of PANI, TiO₂ and SnO₂ in the composite of PANI-SA•TiO₂-SnO₂(10%).

Electrochemical performance of polyaniline–metal oxide composites

A supercapacitor can be classified into two major categories based the mechanism; one is electrochemical double layer capacitor (EDLC), and the another one is pseudocapacitor (*pC*). EDLC is suffering from energy density, and pseudocapacitor is suffering from the stability point of view. Mostly used *pC* materials are polyaniline and metal oxides. Polyaniline shows higher capacitance and metal oxide gives the stability. Hence, in this work, we find the electrochemical performances of composites of polyaniline with the metal oxide. We selected SnO₂ and TiO₂ for metal oxide category and polyaniline in conducting polymers. Initially, we carried out the cyclic voltammetric studies for PANI-SA and polyaniline composites with TiO₂/SnO₂/TiO₂-SnO₂.

Voltammogram patterns and their corresponding specific capacitance values for the samples, TiO₂-SnO₂(10%), PANI-SA, PANI-SA•SnO₂, PANI-SA•TiO₂ and PANI-SA•TiO₂-SnO₂(10%), were found from cyclic voltammetric experiments. CV was carried in symmetric cell configuration containing two electrodes of identical sample in 1 M aqueous sulphuric acid electrolyte in

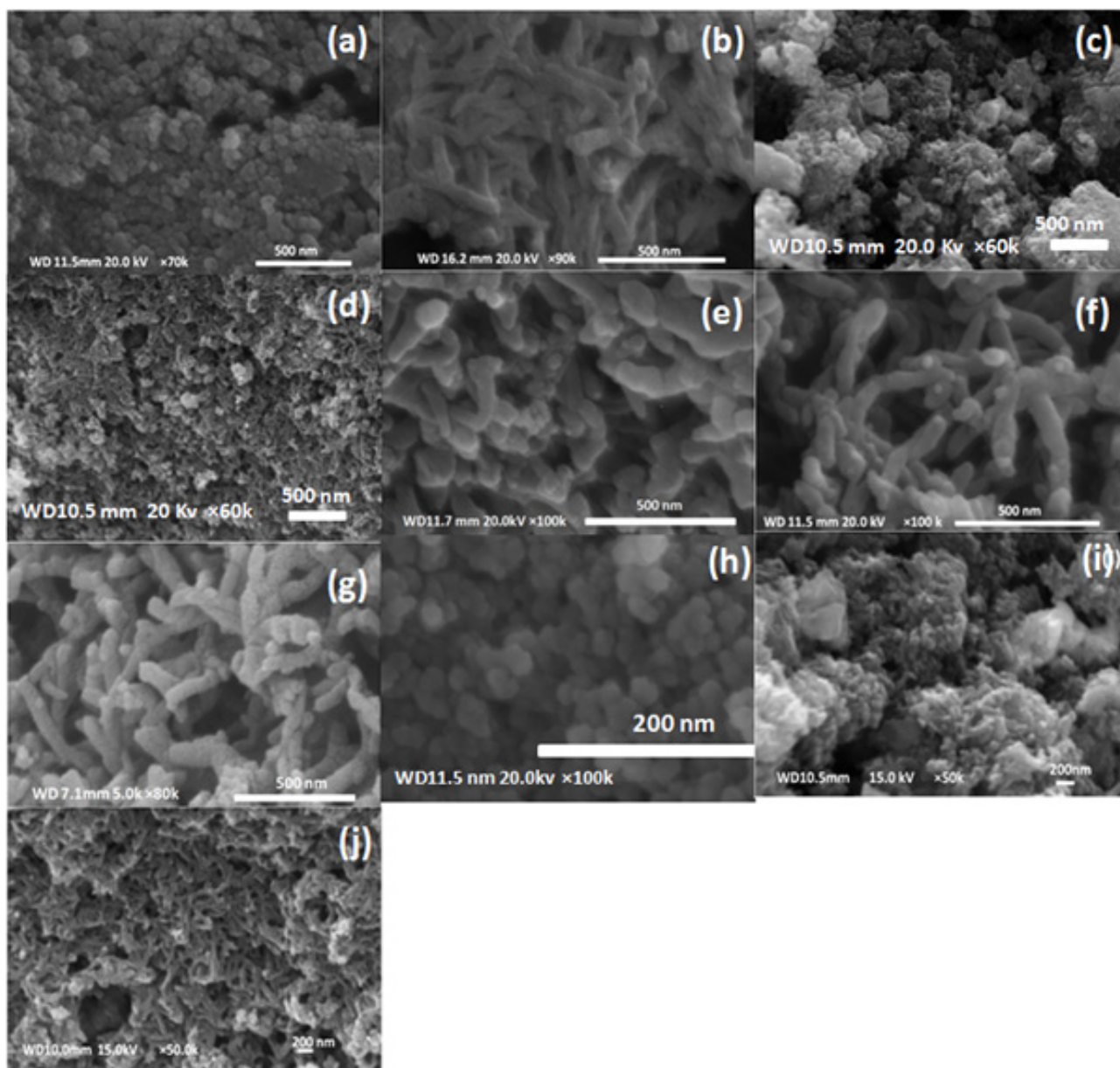


Figure 3. SEM images at 500 nm scale (a) $\text{TiO}_2\text{-SnO}_2(10\%)$, (b) PANI-SA, (c) PANI-SA• SnO_2 , (d) PANI-SA• TiO_2 , (e) PANI-SA• $\text{TiO}_2\text{-SnO}_2(5\%)$, (f) PANI-SA• $\text{TiO}_2\text{-SnO}_2(10\%)$, and (g) PANI-SA• $\text{TiO}_2\text{-SnO}_2(15\%)$; at 200 nm scale, (h) $\text{TiO}_2\text{-SnO}_2(10\%)$, (i) PANI-SA• SnO_2 , and (j) PANI-SA• TiO_2 .

the voltage range of -0.2 to 0.6 V at a scan rate of 10 mV s^{-1} . The results are depicted in Figure 5.

Sample containing polyaniline shows oxidation and reduction peaks, indicating pseudocapacitive behaviour. $C_s(\text{CV})$ value of mixed metal oxide [$\text{TiO}_2\text{-SnO}_2(10\%)$] was found as 15 F g^{-1} , whereas, polyaniline salt showed a higher value of $C_s(\text{CV})$ [250 F g^{-1}]. Conducting polymers are generally attractive as they have high charge density and low cost (compared with the relatively expensive metal oxides).^[35]

The $C_s(\text{CV})$ value of polyaniline salt increases with the use of metal oxide $\text{SnO}_2(315 \text{ F g}^{-1})$ or $\text{TiO}_2(375 \text{ F g}^{-1})$, and the $C_s(\text{CV})$ of polyaniline salt with mixed metal oxide was higher (485 F g^{-1}) than that of polyaniline salt composite with single metal

oxide. Supercapacitor cell of PANI-SA• $\text{TiO}_2\text{-SnO}_2(10\%)$ was subjected at increasing scan rates of 1, 5, 10, 20, 30, 40, 50 and 100 mV s^{-1} and their corresponding $C_s(\text{CV})$ values are decrease as 585, 460, 482, 445, 428, 420, 406 and 380 F g^{-1} respectively and this is obvious results.

To confirm the trend of the $C_s(\text{CV})$ results from the CV, we carried charge-discharge experiments for the samples, $\text{TiO}_2\text{-SnO}_2(10\%)$, PANI-SA, PANI-SA• SnO_2 , PANI-SA• TiO_2 and PANI-SA• $\text{TiO}_2\text{-SnO}_2(10\%)$. $C_s(\text{CD})$ values were determined in symmetric cell configuration containing two electrodes of identical sample in 1 M aqueous sulphuric acid electrolyte in the voltage range of 0 to 0.6 V at a current density of 0.35 A g^{-1} (Figure 6). $C_s(\text{CD})$ value of mixed metal oxide [$\text{TiO}_2\text{-SnO}_2(10\%)$] was found

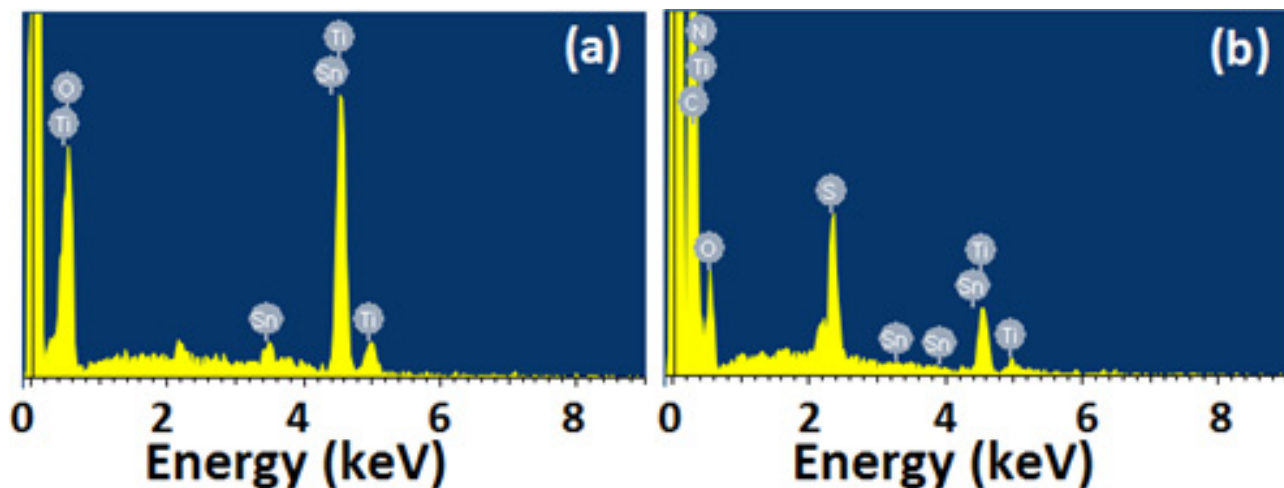


Figure 4. EDAX spectra of (a) TiO₂-SnO₂(10%), (b) PANI-SA•TiO₂-SnO₂(10%).

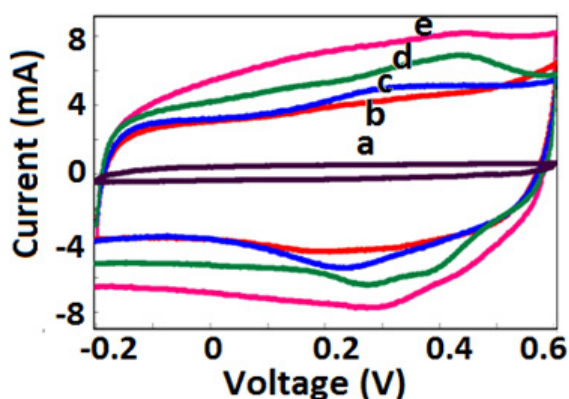


Figure 5. Cyclic voltammograms of (a) TiO₂-SnO₂(10%), (b) PANI-SA, (c) PANI-SA•SnO₂, (d) PANI-SA•TiO₂ and (e) PANI-SA•TiO₂-SnO₂(10%) at 10 mV s⁻¹ potential sweep rate..

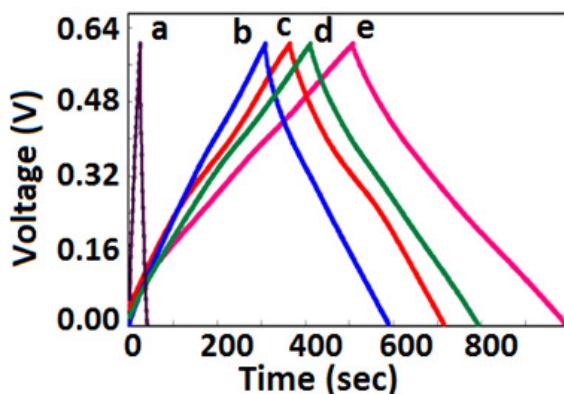


Figure 6. Charge-discharge curves of (a) TiO₂-SnO₂(10%), (b) PANI-SA, (c) PANI-SA•SnO₂, (d) PANI-SA•TiO₂ and (e) PANI-SA•TiO₂-SnO₂(10%) at 0.35 A g⁻¹ current density.

as 10 F g⁻¹, whereas, polyaniline salt showed a higher value of C_s(CD) [(310 F g⁻¹)]. The C_s(CD) value of polyaniline salt

increases with the use of metal oxide SnO₂ (385 F g⁻¹) or TiO₂ (420 F g⁻¹), and with mixed metal oxide [TiO₂-SnO₂(10%)] was higher (540 F g⁻¹) than that of single metal oxide composite.

Specific capacitance value for the composite of polyaniline with mixed metal oxide calculated from cyclic voltammetry or charge-discharge experiments was found higher than that of its individual components. Hence, C_s(CV)/ C_s(CD) values of polyaniline mixed metal oxide composite were determined by varying the amount of SnO₂ in the mixed metal oxide. The values are represented in Figure 7. As a representative system, C_s(CV) value calculated at a sweep rate of 1 mV s⁻¹, increases with increase in the content of SnO₂ in the mixed metal oxide, attains a maximum (585 F g⁻¹) at 10 wt.% of SnO₂, and further increase in the content of SnO₂, resulted in decrease in C_s(CV) value. (Figure 7A). Another observation is that the C_s(CV) decreases with increase in the scan rate. A similar result was obtained from CD experiment carried out at a discharge current of 1, 2 and 5 mA. (Figure 7B).

The CV and CD experiments carried for the polyaniline composites with increasing the amount of SnO₂ in TiO₂-SnO₂, showed that PANI-SA•TiO₂-SnO₂(10%) is having higher electrochemical performance. For optimization of mixed metal oxide and polyaniline proportions in the composites, PANI-SA•TiO₂-SnO₂(10%) composites were prepared by varying the amount of mixed metal oxide [TiO₂-SnO₂(10%)] (i.e., 50 mg, 100 mg, 150 mg, 200 mg, 500 mg) via the above procedure and calculated the specific capacitance values from charge-discharge experiments at 0.35 A g⁻¹ current density and the values are 450, 540, 520, 480, 400 F g⁻¹ respectively. Further, the value of C_s(CD) for PANI-SA•TiO₂-SnO₂(10%) was carried at increasing current densities of 0.35, 0.7, 1, 1.7, and 3.5 A g⁻¹ (Figure 8A) and are found to be 540, 518, 486, 440 and 365 F g⁻¹ respectively. This result shows that the sample withstands even at higher CD current density of 3.5 A g⁻¹. The specific capacitance decreased with increasing charge-discharge current density. Generally, the electrolyte ions could not enter the internal structure of the electro-active material at a higher

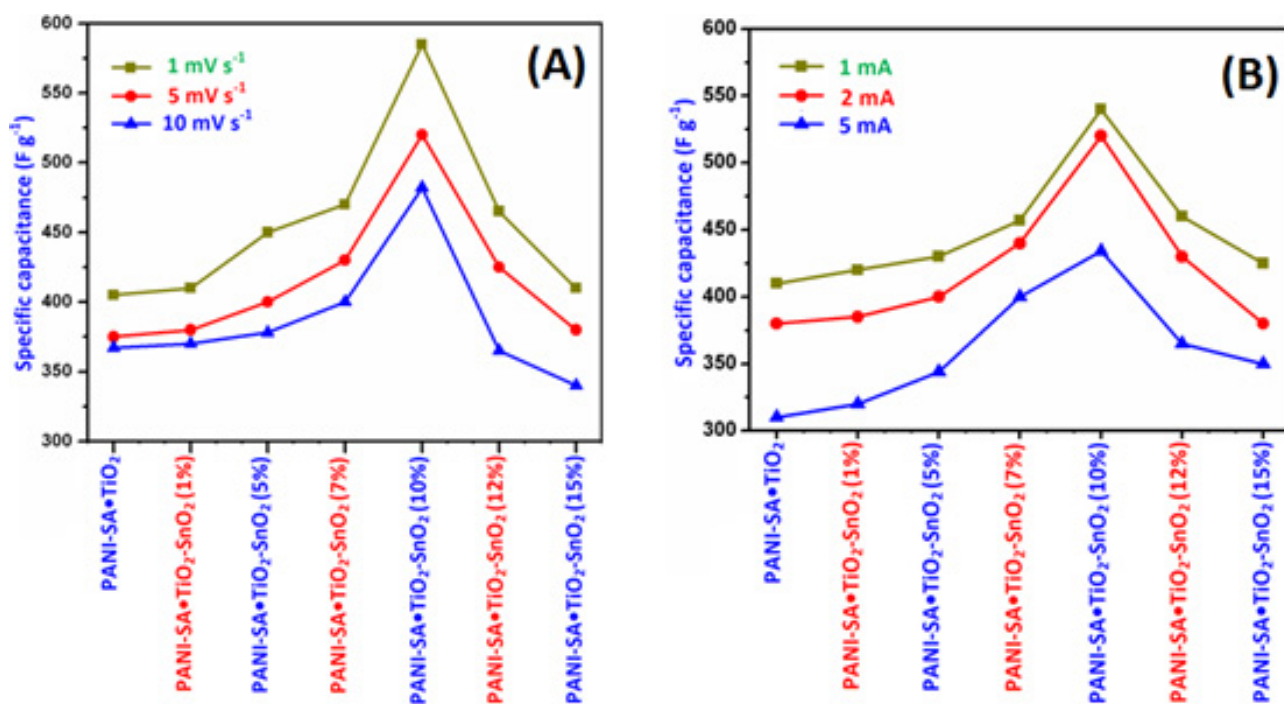


Figure 7. Specific capacitances of PANI-SA•TiO₂-SnO₂ composites (A)From CV studies at different sweep rates. (B)From CD studies at different current densities.

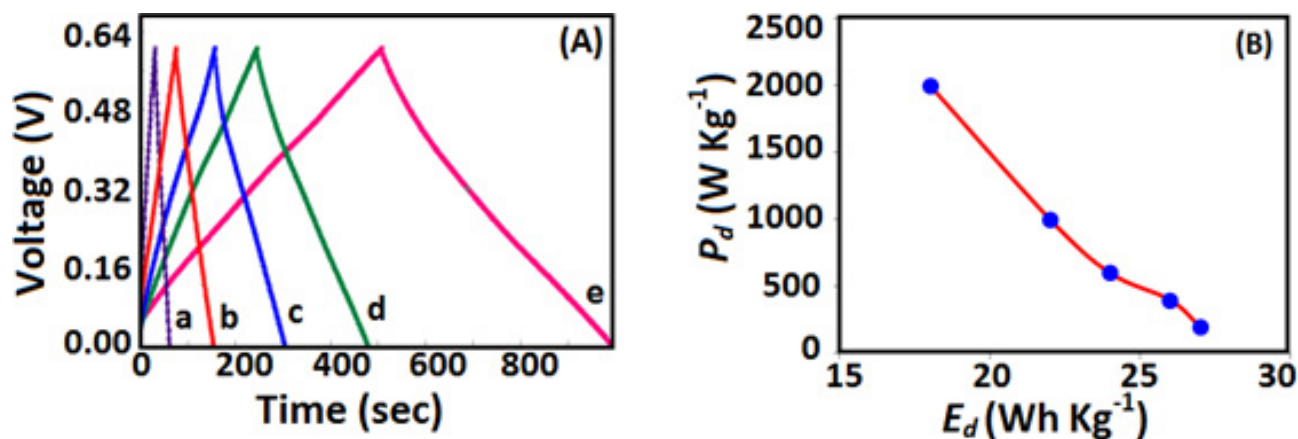


Figure 8. (A) Charge-discharge studies of PANI-SA•TiO₂-SnO₂(10%) at various current densities of (a) 3.5, (b) 1.7, (c) 1, (d) 0.7 and (e) 0.35 A g⁻¹ and (B) their corresponding Ragone plot..

current density.^[36] Energy density and power density are the two important performance indicators for energy storage devices. The Ragone plot of a capacitor shows the relation between the energy-storage and power capabilities of the capacitor. The Ragone plot of supercapacitor with PANI-SA•TiO₂-SnO₂(10%) electrodes shown in Figure 8B.

Energy density values are 27, 26, 24, 22, and 18 Wh kg⁻¹ with the corresponding power density values of 200, 400, 600, 1000 and 2000 W kg⁻¹. Notably, this symmetric supercapacitor can deliver a high energy density of 27 Wh kg⁻¹ at a power density of 200 W kg⁻¹, and the energy density still retains 18 Wh kg⁻¹ with a higher power density of 2000 W kg⁻¹. This high

rate capability makes this material suitable for high power supercapacitor applications.

The stability of the supercapacitor based on PANI-SA•TiO₂-SnO₂(10%) composite during long-term charge-discharge cycling is one of the most significant factors for its practical applications. PANI-SA•TiO₂-SnO₂(10%) system was subjected to 6000 galvanostatic charge-discharge cycles at a current density of 0.35 A g⁻¹ and its corresponding specific capacitance, coulombic efficiency and equivalent series resistance (ESR) are shown in Figure 9. The supercapacitor maintained 85% of its original capacitance (540 F g⁻¹) after 6000 cycles, indicating good capacity retention. Coulombic efficiencies are found to be

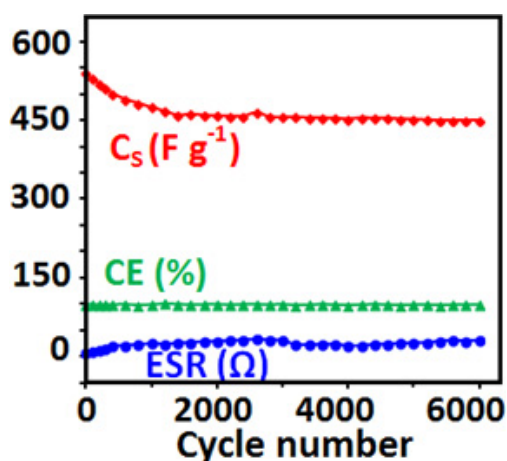


Figure 9. Specific capacitance, coulombic efficiency and ESR of PANI-SA•TiO₂-SnO₂(10%) electrode with charge-discharge cycles at a current density of 0.35 A g⁻¹.

Electrochemical impedance spectroscopy (EIS) was used to understand the ion-transfer behavior, electrical resistance and frequency response behaviours of the electrode materials. EIS experiments were carried for the electrodes of PANI-SA•TiO₂-SnO₂(10%), PANI-SA•TiO₂, PANI-SA•SnO₂, PANI-SA in the frequency range of 40 kHz–10 mHz at an applied voltage of 0.6 V. The Nyquist and bode plots are shown in Figure 10. This Nyquist plot consists of a depressed semicircle in the high frequency region and a near vertical line in the low frequency region. The values of charge-transfer resistance and time constant were calculated from the semicircle and specific capacitance [C_s (EIS)] was calculated in the low frequency region. The results are reported in Table 2. The hybrid, PANI-SA•TiO₂-SnO₂(10%) shows low charge-transfer resistance (0.8 Ω) and time constant (0.2 ms) with a higher specific capacitance value of 416 F g⁻¹. Also it shows a phase angle of 82°, which is close to that of an ideal supercapacitor value of 90°.

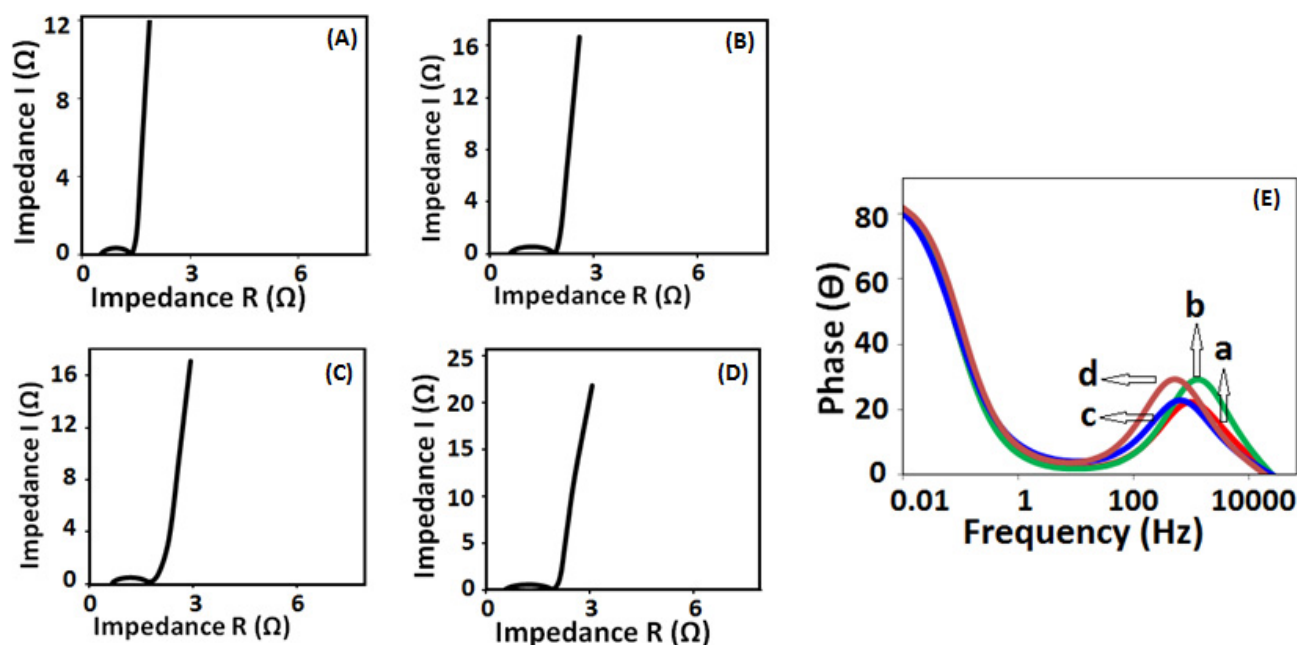


Figure 10. Nyquist plots of (A) PANI-SA•TiO₂-SnO₂(10%), (B) PANI-SA•TiO₂, (C) PANI-SA•SnO₂, (D) PANI-SA and (E) Bode plots of respective samples at 0.6 V voltage in the frequency range of 40 kHz-10 mHz.

Table 2. Charge-transfer resistance (R_{ct}), time constant (τ), specific capacitance [C_s (EIS)] and Phase angle (θ) values of polyaniline-metal oxide composites				
System	R_{ct} (Ω)	τ (ms)	C_s (EIS)(F g ⁻¹)	Phase angle (θ)
PANI-SA•TiO ₂ -SnO ₂ (10%)	0.8	0.2	416	82
PANI-SA•TiO ₂	1.2	0.2	318	81
PANI-SA•SnO ₂	1.2	0.4	310	80
PANI-SA	1.3	0.6	243	81

constant with cycle numbers (97-100%). Equivalent series resistance (ESR) value increases slightly from 5 to 30 Ω at the end of 6000 cycles.

The operating frequency (The frequency at which the capacitance is 50% of its maximum value) of PANI-SA•TiO₂-SnO₂(10%), PANI-SA•TiO₂, PANI-SA•SnO₂ and PANI-SA is found to be 3 Hz, 4 Hz, 1.5 Hz and 2.5 Hz respectively.

The improved electrochemical performance of composite of polyaniline with mixed metal oxide compared to that of polyaniline and its composite with metal oxide are may be due to (i) higher electron transfer rate

due to reduction in band gap and (ii) more space between the nano rods, which allow the electrolyte to interact more surface of the electrode. One of the band gaps of polyaniline salt is at 3.35 eV, and this band gap of polyaniline salt is shifted to 3.1 eV in the composite of PANI with SnO₂.^[37] In the case of PANI-TiO₂, PANI peak at band gap of 3.35 eV and TiO₂ (3.2 eV) become 3.0 eV.^[5] Similarly, the band gap of mixed metal oxide of TiO₂-SnO₂ decreases very significantly to 2.5 eV compared to the individual metal oxide band gap of TiO₂ (3.2 eV) and SnO₂ (3.6 eV).^[38,39] Thus in the case of the composite of PANI with mixed metal oxide, the electron transfer rate may be higher, which in turn result in higher electrochemical performance.

Electrochemical performances of composite of polyaniline and metal oxides have been studied towards the use in supercapacitor. Most of the reports, electrochemical performance have been carried out via three electrodes configuration (Table 1). However, for practical application, it should be carried out in two electrodes via cell configuration. Generally, electrochemical performances of single electrode will be higher than that of the electrode in cell configuration. In this work, composite of polyaniline with mixed metal oxide (PANI-SA•TiO₂-SnO₂) is used as electrode in symmetric supercapacitor cell configuration. This system showed better electrochemical performance in terms of specific capacitance (540 F g⁻¹), energy density (27 Wh Kg⁻¹) at power density (200 W Kg⁻¹), cycle stability (6000 cycles with 85% retention in capacitance), low charge transfer resistance, good frequency range etc. at 0.6 V. The performances of PANI-SA•TiO₂-SnO₂ are higher than that of the performances of reported system for PANI-SnO₂ as 501 F g⁻¹, 2000 cycles at 0.5 V^[30] and PANI-TiO₂ system, which showed 355 F g⁻¹, 1700 cycles at 0.6 V.^[17]

Conclusion

Organic-Inorganic hybrid, PANI-SA•TiO₂-SnO₂, was synthesized by the chemical oxidative polymerization of aniline in presence of metal oxide. For comparison, polyaniline salt containing metal oxide, i.e. PANI-TiO₂ and PANI-SnO₂ were also prepared. Formation of polyaniline salt containing metal oxide was supported by FT-IR, XRD and EDAX results. These composite materials were used as electrode in supercapacitor application. Electrochemical performances of these composite electrodes were carried from cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy. The specific capacitance value of polyaniline-mixed metal oxide composite was higher (540 F g⁻¹) than that of its metal oxide composite, PANI-TiO₂ (420 F g⁻¹) and PANI-SnO₂ (365 F g⁻¹) at a power density of 200 W kg⁻¹. PANI-SA•TiO₂-SnO₂ (10%) composite showed 85% retention of its original capacitance value of 540 F g⁻¹ at 6000 charge-discharge cycles. Polyaniline mixed metal oxide composite was even stable at higher power density of 2000 W kg⁻¹. This study reports a promising and efficient way to obtain excellent electrode materials for energy storage devices with high performance.

Supporting Information

Experimental section, Instrument details used for Characterizations (i.e., FTIR, XRD, FESEM and EDAX) and formulas used in electrochemical studies (i.e., CV, CD and EIS).

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Electrochemistry · Energy storage · Impregnation method · Mixed metal oxide · Polyaniline

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