# Ternary hybrid electrode material based on polyaniline/carbon nanohorn/TiO<sub>2</sub> with high performance energy storage capacity

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# Abstract

Renewable energy is very much demanding in modern time. Herein, we have discussed energy storage performance of polyaniline (PANI) and carbon nanohorn (CNH) decorated titanium dioxide (TiO<sub>2</sub>) nanoparticle, high performance electrode material. This high performance energy storage material was prepared through simple and cost effective method via in-situ polymerization of aniline in presence of CNH and TiO<sub>2</sub> nanoparticles. Thus, as prepared active electrode material provide high specific capacitance value of 1068 F/g at current density of 3 A/g. The existence TiO<sub>2</sub> nanoparticle in the ternary hybrid leads to enhancement of capacitance value through synergistic effect compared to the pure components (e.g., PANI and CNH are 335 F/g and 240 F/g, respectively at same current density). As morphological analysis says, TiO<sub>2</sub> nanoparticles are observed to be coated by CNH nanofiller and PANI fiber in the hybrid, which plays a key role to enhance the capacitance value of hybrid making it highly promising electrode material for energy storage in next generation power supply. Copyright © 2018 VBRI Press.

Keywords: Supercapacitor, polymer hybrid composite, high energy storage, polyaniline, carbon nanohorn, TiO<sub>2</sub>

# Introduction

Renewable energy is most promising energy source in present time due to lack of fossil fuels. For alternating energy source, researchers are highly concentrated on supercapacitor electrode materials for their high performance activities [1-3]. Due to high power density, fast charging/discharging ability, high cyclic efficiency, supercapacitor electrode materials are hugly accepted in modern high performance digital area [4,5]. Thus, supercapacitor materials have been alternative energy source for portable devices, electronics cars, and electronics gazettes etc. Electrical double-layer capacitors (EDLCs) and pseudocapacitors are basically two different types of supercapacitors, for developing energy [6,7]. Among them, pseudocapacitors are considered most promising and futurities energy storage electrode material for their high performance activities. Several research works are already reported on the conducting polymer or carbon nanofiller based supercapacitor materials [8-17]. In this case, active electrode materials will perform both as EDLC and pseudocapacitor which will enhance the supercapacitor performance significantly [18-22]. Among transition metal oxides, TiO<sub>2</sub> nanoparticles have attracted attention for energy storage due to its long-term thermodynamic stability, strong oxidizing power and nontoxicity. TiO<sub>2</sub> nanoparticle based supercapacitor electrode materials reported earlier. However, they will not achieve high capacitance value. For instance, Zhang et al. **[23]** prepared multifunctional TiO<sub>2</sub>/graphene nanocomposites hydrogel by facile one-pot hydrothermal method. They reported the specific capacitance value of the nanocomposite as 206.7 F/g at 0.5 A/g current density. Ramadoss et al. **[24]** reported hydrothermal fabrication of porous two-dimensional (2D) reduced grapheme oxide/TiO<sub>2</sub> nanorod array/reduced graphene oxide (rGO/TiO2 NR/rGO) which delivers 114.5 F/g at scan rate of 5 mV/s. Sun et al. **[25]** have studied the electrochemical properties of TiO<sub>2</sub>/graphene composites which show specific capacitance value of 84 F/g at 10 mV/s scan rate. Deshmukh et al. **[26]** have synthesized Fe<sub>3</sub>O<sub>4</sub>/SWCNH nanocomposites and obtained the specific capacitance value of 377 F/g at the current density of 1A/g.

In this present study, we report the synthesis and electrochemical characterization of hybrid electrode material (PTC) with high energy storage capacity. This work is combination of pseudocapacitive behavior of TiO<sub>2</sub> nanoparticle and PANI along with the double layer capacitance of CNH. The ternary hybrid was synthesized through *in-situ* polymerization of aniline in presence of conducting CNH and TiO<sub>2</sub> nanoparticles. The reason behind the choosing of CNH is that it has large surface area with high aspect ratio, inherent micropores at interstitial sites, high electrical conductivity, excellent porosity and considerable internal nanospace. In the hybrid material, TiO<sub>2</sub> nanoparticles are coated by

conducting CNH nanofiller along with PANI fiber, which facilitates the electron transport phenomena by reducing resistance and thereby the ultimate capacitance value of the hybrid is greatly enhanced. Finally, the ternary hybrid shows high capacitance value of 1068 F/g at current density of 3 A/g, being far higher value compared to the pure PANI (335 F/g) and CNH (240 F/g) at the same current density (3 A/g). Thus, TiO<sub>2</sub> effectively plays an important role to enhance the capacitance value of the ternary hybrid material.

# **Experimental and characterizations**

## Materials details

Aniline, hydrochloric acid (HCl) and potassium chloride were purchased from Merck, Germany. TiO<sub>2</sub> nanoparticle was purchased from sigma Aldrich (average size ~21 nm and B.E.T. surface rarea ~49 m<sup>2</sup>/gm). Single-layer carbon nanohorn (CNH, carbon purity: > 99%, horn diameter: 3~5 nm, horn length: 30~50 nm, cluster diameter: 60~120 nm, density: 1.1 g/cm3, surface area: 250~300 m<sup>2</sup>/g) was procured from J. K. Impex, Mumbai, India. Cetyl trimethylammonium bromide (CTAB) and ammonium persulfate (APS) [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] were purchased from Loba Chemie Pvt. Ltd. India.

# Preparation of the PTC hybrid

At the start, 100 ml 1.5 (M) HCl was taken in a 500 ml beaker and then, 30 mg of CNH and CTAB were added to that acid solution. Then, the mixture was sonicated under ultrasound for 1h to have homogeneous dispersion of CNH in the solution, followed by vigorous stirring for another 30 min with magnetic stirrer at room temperature. In another beaker, 150 mg of TiO2 nanoparticles were dispersed in de-ionized water and this dispersed TiO<sub>2</sub> nanoparticles were added to that stirring solution and the whole mixture was ultra-sonicated for around 30 min followed by magnetically stirring for another 40 min at room temperature. Finally, 1ml aniline was added to that dispersed mixture of CNH and TiO<sub>2</sub> followed by addition of ammonium persulfate (APS) solution (prepared by dissolving 2 gm of APS in 100 ml 1.5 (M) HCl) under vigorous stirring condition. Here, APS acts as an oxidizing agent for polymerization of aniline. After 6h of reaction, the solution became greenish and then filtered. The residue was washed with de-ionized (DI) water and absolute ethanol for several times to remove excess acidic content. Finally, the obtained greenish residue was air dried for 24 h prior to further characterizations. Polyaniline (PANI) was also synthesized by in-situ polymerization of aniline using the same method for comparison study. A schematic representation for the preparation of PTC hybrid is shown in Fig. 1.

### Field Emission Scanning Electron Microscope (FESEM) and High Resolution Transmission Electron Microscope (HRTEM)

FESEM study of the PTC hybrid was carried out for morphological analysis through FESEM (FE-SEM, Carl

Zeiss-SUPRA<sup>TM</sup> 40), with an accelerating voltage of 5kV. The sample was prepared by homogeneous dispersion of small amount powder sample in ethanol and then, only one drop of that dispersed material was casted onto the clean Al-foil. The samples were coated with a thin layer of gold (approx ~ 5 nm) to avoid the electrical charging and were scanned in the vacuum order of ~10<sup>-4</sup> to ~10<sup>-6</sup> mm Hg. The HRTEM analysis of the PTC hybrid was done by HRTEM (HRTEM, JEM-2100, JEOL, JAPAN), operated at an accelerating voltage of 200 kV. A very minute amount of the PTC hybrid was dispersed homogeneously in ethanol by ultra-sonication and that dispersed suspension was dropped on the copper (Cu) grid for HRTEM analysis.

# Electrochemical characterization

Electrochemical analyses of PTC hybrid, CNH and pure PANI were done by CH instrument electrochemical analyzer with three-electrode system where PTC hybrid coated glassy carbon electrode (GCE), Pt wire and Ag/AgCl served as working, counter and reference electrode, respectively. Cyclic voltammogram (CV) was recorded at various scan rates (5, 10, 20, 30, 50, 60, 80 and 100 mV/s) within the potential window from – 0.4 to + 0.8 V in 1 (M) KCl electrolyte. The specific capacitance values ( $C_{sp}$ ) of PTC hybrid (0.12 mg) were estimated using the following relation at various scan rates: [27]

$$C_{sp} = \left(\int IdV\right) / vmV \tag{1}$$

where, *I* is the response current, *V* is the potential range (V), *v* is the potential scan rate (mV/s) and *m* is the mass of the PTC hybrid in the electrodes. The electrochemical impedance spectroscopy (EIS) was measured in the frequency range of 100 mHz – 1 MHz.



PTC hybrid

Fig. 1. Schematic representation for the preparation of PTC hybrid.

# **Results and discussion**

# Morphology study

The different types of morphological analyses were carried out for pure PANI, CNH and PTC hybrid and Fig. 2 represents different morphological images.



Fig. 2. FESEM micrographs of (a) pure PANI, (b) CNH and (c, d) PTC hybrid and HRTEM micrographs (e, f) of PTC hybrid.

Fig. 2a shows the FESEM image of pure PANI. This image (Fig. 2a) confirms the fiber-like image of PANI. FESEM image of the nanofiller CNH is observed in Fig. 2b wherefrom the flower-like morphology is clearly observed. Two FESEM images have been recorded for PTC hybrid represented by Fig. 2c and 2d, respectively. From these images (Fig. 2c and 2d), it is clearly observed that TiO<sub>2</sub> nanoparticles are coated by conducting CNH nanofillers and surrounded by conducting PANI fiber. Thus, conducting network path is well developed in the PTC hybrid, which will provide more active sites for electron transfer reducing resistance and plays a crucial role to enhance the capacitance value of the hybrid. The  $\pi$ - $\pi$  interaction among the conducting CNH, PANI and TiO<sub>2</sub> nanoparticle also help to increase the capacitance value of the PTC hybrid. The high electrical conductivity of the PTC hybrid is also obtained due to this continuous conducting interconnected network path, which facilitates easy electron transfer throughout the PTC hybrid. The HRTEM images of PTC hybrid are shown in Fig. 2e and 2f at two different magnifications. Both images (Fig. 2e and 2f) confirm the CNH and PANI coated TiO<sub>2</sub> nanoparticles in PTC hybrid which plays a crucial role to enhance the capacitance value as well as electrical conductivity of the PTC hybrid.



**Fig. 3.** CV plots of (a) pure PANI, (b) pure CNH, and (c) PTC hybrid at different scan rates and (d) variation of their specific capacitances with scan rates.

### **Electrochemical analysis**

# Cyclic voltammetry (CV) analysis

The cyclic voltammetry tests of all electrode materials (pure PANI, pure CNH, and PTC hybrid) have been carried out within potential window from -0.4 to +0.8 V using 1 (M) KCl as the electrolyte in three electrode system. Fig. S2 (in supporting information) shows the CV curves of bare GCE, pure PANI, pure CNH, and PTC hybrid at 5 mV/s scan rate. Pseudocapacitive nature of PANI and PTC, indicating by non-rectangular shape and CNH shows EDLC character (rectangular shape), as shown in Fig. S2 (in supporting information). CV analysis shows that the reduction and oxidation process occurred in cathode and anode, respectively which generates negative and positive current in the cyclic voltamogram. The higher area under the CV curve of PTC is the consequence of its higher current response, which enables it to have higher specific capacitance (C<sub>sp</sub>) than the rest electrode materials. The obtained C<sub>sp</sub> value is 1088 F/g, respectively for PTC hybrid at 5 mV/s scan rate [as per the calculation using equation (1)]. This higher  $C_{sp}$  value obtained for the PTC hybrid indicates the intimate interaction among PANI, TiO2 and CNH that increase the charge transfer between the components in the composites. The deviation of cyclic voltammogram for PTC hybrid from the ideal one indicates pseudocapacitive behavior exhibited by TiO<sub>2</sub>, making the C<sub>sp</sub> value higher, i.e., TiO<sub>2</sub> undergoes some redox reactions in that electrolyte, and thereby making some contribution to the total specific capacitance value of the PTC hybrid. Moreover, the effective charge transfer in the electrode plays an important role for easy and fast ion transport in the electrode material and enhances the C<sub>sp</sub> value of the PTC hybrid. In the PTC hybrid, the  $\pi$ - $\pi$  stacking interaction among CNH nanofiller, TiO<sub>2</sub> nanoparticles and electron rich PANI chains plays a synergistic effect to the electrochemical properties in the PTC hybrid [29, 30]. This may be attributed to decrease internal resistance compared to the electrode made of only PANI. So, these results lead us to conclude that TiO<sub>2</sub> nanoparticle in the PTC hybrid plays an important role in the presence of CNH and PANI to improve the capacitance value and finally high capacitance value (1088 F/g at 5 mV/s scan rate) is achieved for PTC hybrid. The capacitive behavior of the entire electrode materials were also examined at various scan rates ranging from 5 mV/s to 100 mV/s, as displayed in **Fig. 3.** Here, it is noteworthy that both the intensities of the peaks and their separation get increased with increase in scan rate describing the enhanced over potentials **[31]**. The PTC hybrid can be considered to be appreciably stable as it produces redox peak even at high scan rate like 100 mV/s.

The relation of specific capacitance values with the scan rates for all the electrode materials is shown in Fig. 3d. Here, actually the specific capacitance values were measured at various scan rates (5, 10, 20, 30, 50, 60, 80 and 100 mV/s) and plotted against the respective scan rates. Interestingly, the capacitance values of every material gradually decreased with increasing the scan rate and this is the general trend. At high scan rate, large electrochemical polarization and high diffusion resistance affect the electrode material, which, in turn, lead to decrease in the capacitive performance of the hybrid [32]. For any supercapacitor, the most important part is the electrode material. Therefore, in recent times, the researchers are mainly interested on the preparation and design of the electrode material. Now, the following four points are mainly considered or maintained while fabricating an electrode material: power density, energy density, low weight and high structural stability. Now, power density is directly related to transport kinetics. Therefore, use of meso- or nanoporous carbonaceous materials (CNT, graphene, CNH etc.) is recommended as these ensure maximum contact with electrolyte. Use of conducting material like conducting polymers (polypyrrole, polyaniline, PEDOT etc.) also gives some conductivity to the electrode material, facilitating the transport of ions and electrons through it and hence enhancing the extent of electrochemical reaction and power density. As  $E = (1/2) CV^2$ , so, use of the materials having higher capacitance value with large working voltage range increases the energy density.

For this, transition metal oxides or hydroxides and conducting polymers are very helpful. Light weight electrode materials increase the energy and power densities as their units are Wh/kg and W/kg, respectively and also those can be applied in mobile or portable electronics. Since, supercapacitors undergo through thousand and thousand cycles of charging and discharging (CCD), it should have appreciable structural stability to avoid its degradation during CCD. So, to combine all these above strategies together, we have synthesized the composite electrode material based on PANI, TiO<sub>2</sub> and CNH. Here, our attempt is to utilize the individual contribution of each constituent synergistically, where one's weakness is suppressed by another.

In this study, CNH actually shows EDLC behavior, therefore it cannot produce much more specific capacitance and if PANI is solely used, its polymeric backbone may be degraded during CCD. CNH gives stability to PANI backbone along with conductivity to the composite electrode material and also its nanostructure makes the material light weight. Moreover its high surface area facilitates the electrochemical reaction leading to have higher specific capacitance. On the other hand,  $TiO_2$  shows pseudo capacitance making specific capacitance higher, but its lower conductivity leads it to have low power density, but when, it is coupled with conducting polymer like PANI and CNH, facilitated electrochemical reaction to higher extent due to higher kinetic potentials of ions and electrons enables it to have higher specific capacitance.

### Constant current charging/discharging (CCD) test

The CCD test is the more important method as it describes the capacitive behavior under constant current conditions. The specific capacitance value ( $C_{sp}$ ) of all the materials has been estimated from the CCD curve by the following equation [33].

$$C_{sp} = \frac{\left(I \times \Delta t\right)}{\left(\Delta V \times m\right)} \tag{5}$$

Where, I stands for applied current,  $\Delta V$  represents the potential window and  $\Delta t$  signifies for discharge time in seconds and m denotes the active mass of the electrode material, respectively.





**Fig. 4.** CCD curves of pure PANI (a), pure CNH (b), and PTC hybrid (c) at several current densities and variation of their specific capacitances with corresponding current densities (d).

As observable (Fig. 4), the PTC hybrid has attained the higher discharging time and hence displayed higher  $C_{sp}$  of 1068 F/g at 3 A/g whereas the other electrode materials, such as pure PANI and pure CNH show C<sub>sp</sub> values of 335 and 240, respectively. PANI is well known as strong conducting polymer. Due to its porous structure, high surface area, good doping-undoping ability and high charge transfer rate, it behaves as good electrode materials for energy storage applications. Among all these materials investigated, conducting polymers are the most promising as they possess redox pseudo capacitance in addition to double-layer capacitance. However, energy storage performance of PANI itself is not too high. In our case, we have achieved 335 F/g at current density of 3A/g. Due to its excellent properties, we have mixed up PANI with other conducting material and metal oxide to achieve high performance capacitance value. The  $\pi$ - $\pi$ stacking interaction of electron rich PANI polymer with other existing materials in PTC plays a synergistic effect to the electrochemical properties in the PTC hybrid. In addition, PANI which facilitates the electron transport phenomena by reducing resistance and thereby the ultimate capacitance value of the hybrid is greatly enhanced. This improved pseudocapacitive behavior of the PTC hybrid is mainly attributed to the combined

contributions (synergistic effect) of the constituents through mutual interactions which offer this hybrid a large electrode-electrolyte interfacial area available for the redox processes during charging and discharging and to achieve that large  $C_{sp}$  value, appreciable pseudocapacitive character of TiO<sub>2</sub> acts the supreme role too.

The CCD test was also carried out at several higher current densities like 4, 5 and 10 A/g for every electrode sample to set up the consequences of higher current application on their capacitive performance [**Fig. 4**] and the obtained results in the form of a plot were illustrated by **Fig. 4d**. As per the plot, the decreasing trend in the C<sub>sp</sub> values with increase in current density for all the electrode materials [**Fig. 4d**] are perceived owing to lesser availability of redox active sites and limited diffusion of cations within the electrode materials (PANI, CNH, and PTC) were obtained at the current density of 3 A/g within the potential range of - 0.4 V to +0.8 V in the same electrolyte and the corresponding results are recorded in **Fig. S3** (supporting information).

Since, supercapacitor is actually an energy storage device, so the most important part of any supercapacitor, i.e., the electrode material should show significantly high energy density without much deteriorating the power density. In this present work, the energy densities of all the electrode materials along with corresponding power densities were estimated following the equations: [34]

$$E = \frac{1}{2} CV^2 \tag{6}$$

$$P = E/\Delta t \tag{7}$$

Where, *C* (F/g) is the specific capacitance of the electrode material calculated from the CCD plot, *V* (V) indicates the operating voltage and  $\Delta t$  (s) signifies the discharge time obtained from the CCD plot.

Fig. 5a records the variation of energy densities with corresponding power densities (Ragone plot) for all the electrode materials. As per the calculated results, at 3 A/g current density, the highest energy density of about 213.6 Wh/kg with corresponding power density of 1801 W/kg is exhibited by the PTC hybrid while at the highest current density (which has been applied here) of 10A/g, the highest power density of 5996W/kg along with appreciably large energy density of 106.6 Wh/kg has been accomplished. Besides, at similar power densities, no other electrode materials have achieved the energy density higher than that achieved by the PTC hybrid, which definitely ensures its better practical effectiveness as a high-power energy resource. These results are actually the signature of the mutual  $\pi - \pi$  interactions between highly conducting PANI and CNH, which facilitate the electrolytic ion transportation and occurrence of the pseudocapacitive metal oxide, TiO<sub>2</sub> with large C<sub>sp</sub> value within the PTC hybrid.

The long-term cyclic stabilities of all the electrode materials were verified at the current density of 3 A/g in

the same electrolyte and the obtained results are illustrated in Fig. 5b. From the Fig. 5b, it is clearly noticed that the specific capacitance values of all the materials decrease slowly with increasing cycle number and finally the PTC hybrid retains 95% of its specific capacitance after 1000 cycles whereas PANI and CNH display 86%, 84% and retention of their respective specific capacitances. In the PTC hybrid, the strong  $\pi$ - $\pi$ interactions and synergistic contribution of intermolecular interactions among PANI, TiO<sub>2</sub> and CNH make a strong regular network structure that improves the cyclic stability of PTC hybrid. However, the loss in capacitance with increase in cycle number might be due to the mechanical stress generated in PANI backbone during charging and discharging Electrochemical [35]. impedance spectroscopic (EIS) analysis was also carried out for PANI, CNH and PTC hybrid and details description is available in supporting information (Fig. S4 in supporting information).



Fig. 5. (a) Ragone plot of all the electrode materials and (b) cyclic stability test for all the electrode materials at the current density of 3 A/g.

In conclusion, high energy electrode material (PTC hybrid) for supercapacitor application has been prepared through simple and cost-effective in-situ polymerization of aniline in the presence of TiO<sub>2</sub> and CNH nanofiller. The obtained specific capacitance value of the PTC hybrid is very high (1068 F/g at 3A/g). The high specific capacitance value of the hybrid has been obtained due to synergistic contribution of the properties of the components and strong intermolecular  $\pi$ - $\pi$  stacking interactions among the conducting CNH, TiO2 and electron rich phenyl rings of PANI. Thus, the combination of conducting polymer (PANI), conducting nanofiller (CNH) and pseudocapacities of metal oxide (TiO<sub>2</sub>) gives a new promising electrode material for high performance supercapacitor applications. The morphological study, capacitive behavior and electrical properties of the PTC hybrid were studied to support their application area in the field of energy storage. This simple and cost-effective finding would exceptionally help for next generation energy storage and conversion applications. Thus, this highly durable and high performance electrode material could be a very promising as an alternative energy resources for powering up different smart electronics and would be also applicable in future commercial applications.

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### Author's contributions

S. M. and S. K. K contributed equally

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