



Synthesis and Characterization of Polypyrrole-TiO₂ Nanocomposite for Supercapacitor Applications

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Abstract:

In this study, a 5 wt.% TiO₂-loaded polypyrrole (PPy-TiO₂) nanocomposite was synthesized and characterized to evaluate its structural, morphological, and electrochemical properties. The PPy-TiO₂ nanocomposite demonstrated an improved specific capacitance of 117 F/g, highlighting its potential for energy storage applications. The enhanced electrochemical properties can be attributed to the synergistic effects of PPy high conductivity and pseudocapacitance, along with TiO₂ role in enhancing structural stability and charge propagation. These findings suggest that the PPy-TiO₂ nanocomposite is a promising candidate for supercapacitor applications.

Keywords: Polypyrrole; TiO₂; Nanocomposite; Supercapacitor

Introduction:

With the increasing demand for efficient and sustainable energy storage devices, supercapacitors have emerged as promising candidates due to their high-power density, long cycle life, and rapid charge-discharge capabilities. Among the various electrode materials explored for supercapacitors, conducting polymers such as polypyrrole (PPy) have attracted significant attention due to their high conductivity, ease of synthesis, and excellent electrochemical performance. However, pristine PPy suffers from poor cycling stability and limited mechanical strength, restricting its long-term application in energy storage systems.

To overcome these limitations, hybrid nanocomposites incorporating transition metal oxides, such as titanium dioxide (TiO₂), have been widely investigated. TiO₂ is known for its excellent chemical stability, high surface area, and ability to enhance charge storage capacity

through pseudocapacitive behavior. By integrating TiO₂ with PPy, the resulting nanocomposite is expected to exhibit improved electrochemical performance, enhanced charge transport, and better cycling stability. Choudhary et al. [1] reviewed the electrochemical performance of polypyrrole (PPy) and polyindole (PIn) as electrode materials for supercapacitors. PPy offers high flexibility, while PIn ensures long charge retention due to slow hydrolytic degradation. Various polymerization techniques and composite formations with carbon-based and metal-based materials were explored to enhance their properties. The study highlighted the advantages of symmetric and asymmetric supercapacitor configurations using these materials. Their findings suggest that combining PPy and PIn with nanostructured TiO₂ could further improve supercapacitor performance.

Arena et al. [2] developed eco-friendly, low-cost, solid-state supercapacitors on paper substrates with an

areal capacitance of approximately $100 \text{ mF}\cdot\text{cm}^{-2}$. The electrode material was synthesized from a stable water-based ink containing polypyrrole (PPy) doped with dodecylbenzene sulfonic acid (DBSA). The PPy:DBSA ink was applied using rechargeable water pens, forming electrically conductive tracks after drying. A polymer gel based on potassium hydroxide and chitosan was used as both the ion-conducting medium and separator. The study demonstrated that incorporating nanostructured carbon materials further enhanced the capacitance of the supercapacitors. Alam et al. [3] reviewed recent advancements in polypyrrole (PPy) and its composites as electrode materials for asymmetric supercapacitors (ASCs). The study highlights the combination of PPy with materials like activated carbon and transition metal oxides to enhance energy density and electrochemical performance. Various synthesis techniques, including electrochemical deposition and chemical polymerization, have been explored to optimize PPy ASCs' morphology and charge storage capability. The review also discusses the role of nanomaterials and hybrid electrode architectures in improving cycle stability and capacitance. Finally, challenges such as scalability, cost-effectiveness, and real-world integration are addressed, emphasizing PPy ASCs' potential for next-generation energy storage solutions. Gaikar et al. [4] reviewed recent advancements in polypyrrole/manganese oxide (PPy/MnO₂) nanocomposites for thin-film electrodes in supercapacitors. While PPy is widely used for its conductivity and low cost, it faces stability issues over long charge–discharge cycles. MnO₂, known for its high theoretical capacitance and cost-effectiveness, has been explored to enhance PPy's electrochemical performance. The study highlights various chemical synthesis techniques for PPy/MnO₂ composites and their improved specific capacitance and cycling stability.

The findings suggest that these nanocomposites hold promise for next-generation energy storage applications. Jyothibasu et al. [5] reported a facile and eco-friendly approach for fabricating polypyrrole/carbon nanotube (PPyNP/f-CNT) freestanding electrodes for high-performance all-solid-state supercapacitors. The synthesis involved in situ polymerization using curcumin as a bio-template, followed by blending with functionalized CNTs. The composite electrode demonstrated an impressive areal capacitance of 4585 mF cm^{-2} and a volumetric capacitance of 176.35 F cm^{-3} in a three-electrode setup. A symmetric supercapacitor constructed using these electrodes achieved a high areal energy density of $129.24 \text{ }\mu\text{W h cm}^{-2}$, along with 79.03% capacitance retention after 10,000 cycles. These findings highlight the potential of PPyNP/f-CNT composites for next-generation energy storage applications. Wang et al. [6] developed a polypyrrole-based hybrid nanostructure integrating vertical PPy nanotube arrays and carbon nano-onions (CNOs) on textile substrates for wearable supercapacitors. The vertical nanotubes facilitate efficient charge transport, while CNOs enhance conductivity retention during mechanical stretching. A simple template-degrading polymerization method was employed for large-area fabrication. The stretchable supercapacitor exhibited a high specific capacitance of $64 \text{ F}\cdot\text{g}^{-1}$ and outstanding mechanical stability, maintaining 99% capacitance retention at 50% strain after 500 cycles. The study underscores the potential of PPy-based hybrid nanostructures for next-generation wearable energy storage applications. El Nady et al. [7] synthesized a polypyrrole (PPy)/NiO nanocomposite electrode via a one-step electrodeposition technique for supercapacitor applications. The electrode was characterized using FTIR, XRD, SEM, CV, GCD, and EIS techniques. The

PPy/NiO electrode demonstrated a high specific capacitance of $679 \text{ F}\cdot\text{g}^{-1}$ at $1 \text{ A}\cdot\text{g}^{-1}$, with an energy density of $94.4 \text{ Wh}\cdot\text{kg}^{-1}$ and a power density of $500.74 \text{ W}\cdot\text{kg}^{-1}$. The composite electrode retained 83.9% of its initial capacitance after 1000 charge-discharge cycles. The enhanced electrochemical performance was attributed to the synergistic effect of NiO and PPy, forming a porous network structure that facilitated ion transport. This study highlights a facile approach for developing high-performance organic-inorganic hybrid electrode materials for supercapacitors.

In this study, we report the synthesis and characterization of a polypyrrole-TiO₂ (PPy-TiO₂) nanocomposite for supercapacitor applications. The nanocomposite was prepared via in situ chemical polymerization and systematically analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM) and cyclic voltammetry (CV) techniques. The electrochemical performance of the PPy-TiO₂ nanocomposite was evaluated to determine its potential as an advanced electrode material for high-performance supercapacitors.

Experimental Details:

Polypyrrole (PPy), titanium dioxide (TiO₂), and their composite (5 wt.% TiO₂-loaded PPy) were synthesized using an ex-situ approach. The synthesis of polypyrrole was carried out via oxidative chemical polymerization in an acidic medium. Pyrrole monomer (0.5 M) was dissolved in 50 mL of 0.1 M HCl under constant stirring in an ice bath at 5°C to prevent unwanted oxidation. A separate solution of ammonium persulfate (APS, 0.5 M) was prepared in 50 mL of 0.1 M HCl and added dropwise to the pyrrole solution under continuous stirring. The reaction mixture was maintained at 5°C for six hours, leading to the formation of black polypyrrole precipitate. The precipitate was filtered, thoroughly washed with ethanol and

deionized (DI) water, and dried in a vacuum oven at 60°C for 12 hours to obtain pure PPy powder.

Titanium dioxide (TiO₂) nanoparticles were synthesized using a sol-gel method. Titanium isopropoxide (TTIP, 0.1 M) was dissolved in 50 mL of absolute ethanol under continuous stirring. A hydrolysis process was initiated by adding a mixture of deionized water and nitric acid (pH ~2) dropwise to the TTIP solution while stirring at room temperature. The solution was stirred for six hours until a gel-like consistency was achieved. The gel was then aged for 12 hours and dried in an oven at 80°C for 24 hours. The dried gel was ground into a fine powder and subjected to calcination at 400°C for three hours to obtain anatase-phase TiO₂ nanoparticles.

The polypyrrole-TiO₂ composite containing 5 wt.% TiO₂ was prepared using an ex-situ approach. A precise amount of TiO₂ nanoparticles (5 wt.% of the total PPy weight) was dispersed in 50 mL of ethanol using ultrasonication for 30 minutes to ensure uniform dispersion. The pre-synthesized PPy powder was gradually introduced into the TiO₂ dispersion while stirring continuously. The resulting mixture was stirred for 12 hours at room temperature to allow for uniform distribution of TiO₂ within the PPy matrix. The final composite was collected by filtration, washed with ethanol, and dried in a vacuum oven at 60°C for 12 hours.

The synthesized materials were characterized using various analytical techniques. Fourier-transform infrared spectroscopy (FTIR) was employed to confirm the presence of functional groups and interactions between PPy and TiO₂. X-ray diffraction (XRD) was used to determine the crystallinity and phase structure of the materials. Scanning electron microscopy (SEM) provided insights into the surface morphology and dispersion of TiO₂ within the PPy matrix. The electrochemical

performance of the materials was evaluated through cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) techniques using a three-electrode setup in 1 M H₂SO₄ electrolyte. These characterization techniques provided a comprehensive understanding of the structural, morphological, and electrochemical properties of the synthesized PPy-TiO₂ composite for supercapacitor applications.

Results and Discussion:

The XRD pattern (Figure 1) of the 5 wt.% TiO₂-loaded PPy nanocomposite displayed a broad diffraction peak around 2 θ

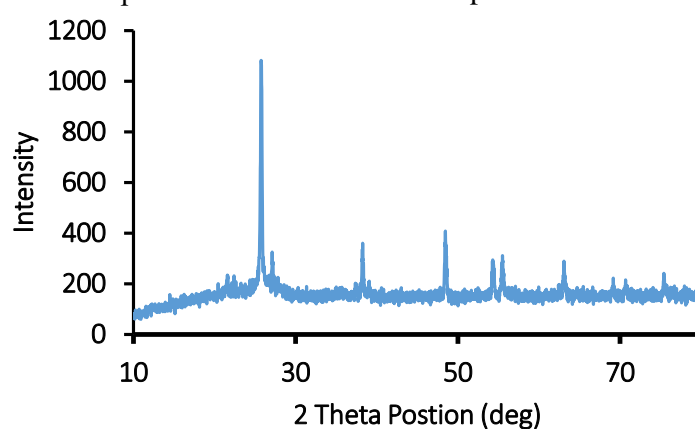


Figure 1. XRD pattern of 5 wt.% TiO₂-loaded PPy nanocomposite.

The SEM images of the 5 wt.% TiO₂-loaded PPy nanocomposite (Figure 2) exhibit a random morphology with irregularly shaped PPy structures. The surface appears rough and non-uniform, with randomly distributed grains and agglomerates. The incorporation of TiO₂ does not significantly alter the fundamental

$\approx 25^\circ$, characteristic of the amorphous nature of polypyrrole. This broad peak indicates the disordered structure of PPy, which is typical for conducting polymers. The absence of sharp crystalline peaks suggests that PPy remains in its non-crystalline phase even after the incorporation of TiO₂. Additionally, the slight broadening of the diffraction peak compared to pristine PPy may be attributed to the interaction between the polymer matrix and the dispersed TiO₂ nanoparticles. No significant crystalline reflections of polypyrrole were observed, further confirming its predominantly amorphous nature.

structure of PPy but introduces slight variations in texture. No well-defined porosity is observed, and the composite retains a disordered arrangement, which is typical for polypyrrole synthesized through chemical polymerization. The absence of a distinct phase separation suggests good dispersion of TiO₂ within the PPy matrix.

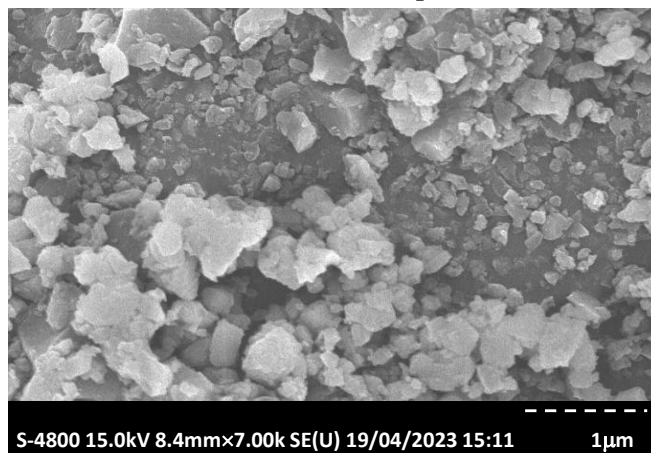


Figure 2. SEM image of 5 wt.% TiO₂-loaded PPy nanocomposite.

The electrochemical performance of the 5 wt.% TiO₂-loaded polypyrrole (PPy-TiO₂) nanocomposite (Figure 3) was evaluated using cyclic voltammetry (CV) in a three-electrode setup. The CV curves displayed a quasi-rectangular shape with slight redox peaks, indicating the contribution of both electrical double-layer capacitance and pseudocapacitive behavior from the redox-active polypyrrole. The absence of significant distortion in the CV profiles suggests good charge propagation within the electrode material. The specific capacitance of the PPy-TiO₂ nanocomposite was calculated using the CV data based on the integrated area under the curve. The

obtained specific capacitance was of the order of 117 F/g, highlighting the enhanced charge storage capability of the composite material. The improved electrochemical performance can be attributed to the synergistic effect of polypyrrole, which provides high conductivity and pseudocapacitance, while TiO₂ enhances structural stability and prevents excessive polymer degradation during charge-discharge cycles. The nearly reversible redox transitions further confirm the material's suitability for supercapacitor applications, ensuring good electrochemical stability and cyclability.

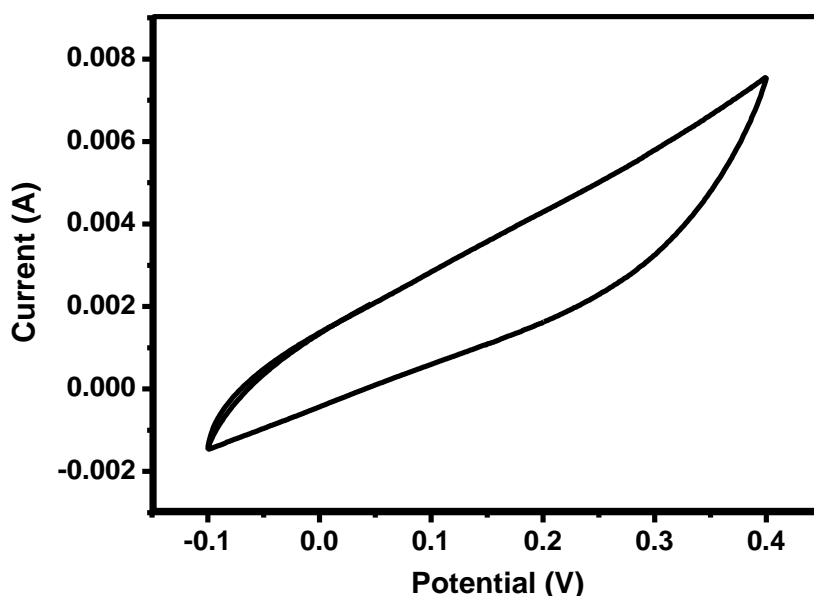


Figure 3. CV curve of 5 wt.% TiO₂-loaded PPy nanocomposite.

Conclusions:

The successful synthesis and characterization of the 5 wt.% TiO₂-loaded polypyrrole nanocomposite demonstrate its potential as an efficient electrode material for energy storage applications. XRD analysis confirmed its predominantly amorphous nature, while SEM imaging revealed a rough, non-uniform morphology with well-dispersed TiO₂ particles. The electrochemical studies showed that the nanocomposite exhibits a favorable capacitance value of 117 F/g with nearly

reversible redox transitions, indicating excellent charge storage capabilities. The synergistic interaction between polypyrrole and TiO₂ contributes to improved electrochemical stability, structural integrity, and cyclability, making it a promising material for supercapacitor applications. Future studies may focus on optimizing the composition and exploring alternative synthesis methods to further enhance its performance.

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