Synthesis of Conducting Bifunctional Polyaniline@Mn-TiO$_2$ Nanocomposites for Supercapacitor Electrode and Visible Light Driven Photocatalysis

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Abstract: We report a polyaniline-wrapped, manganese-doped titanium oxide (PANi/Mn-TiO$_2$) nanoparticle composite for supercapacitor electrode and photocatalytic degradation. The PANi/Mn-TiO$_2$ nanoparticles were synthesized using a solvothermal process, followed by oxidative polymerization of aniline. The structural properties of studied materials were confirmed by XRD, FTIR, HRTEM, FESEM, and UV visible spectroscopy. The as-prepared PANi/Mn-TiO$_2$ nanoparticles revealed admirable electrochemical performance with a specific capacitance of 635.87 F g$^{-1}$ at a current density of 1 A g$^{-1}$ with a notable life cycle retention of 91% after 5000 charge/discharge cycles. Furthermore, the asymmetric cell with PANi/Mn-TiO$_2$ as a positive electrode exhibited energy density of 18.66 W h kg$^{-1}$ with excellent stability. Moreover, the PANi/Mn-TiO$_2$ had promising photocatalytic activity for methylene blue degradation. The improved performance of PANi/Mn-TiO$_2$ nanoparticles is attributed to the well-built synergetic effect of components that lead to significant reduction of band gap energy and charge transfer resistance, as revealed by UV visible spectroscopy and electrochemical impedance spectroscopy.

Keywords: energy storage; bifunctional catalyst; supercapacitor; photocatalyst; PANi/Mn-TiO$_2$

1. Introduction

In response to concerns regarding environmental pollution and depletion of fossil fuel, energy harvesting have been a primary focus across the globe as a sustainable energy resource. Finding an ecofriendly solution to this problem is a hot topic in current scientific research. The ever-growing requirements of portable electronic devices spark intense interest in developing a low cost, pliable, and sustainable energy storage system with high power density, long term stability, and operation security. To meet the energy demand, supercapacitors as energy storage devices are a current focus of attention because of their high-power density, rapid charge-discharge rate, and excellent cycle life stability [1]. Based on charge storage mechanism, supercapacitors are classified into two categories of electric double layer capacitor (EDLC, stores energy as accumulating electric charge at the electrode-electrolyte interface) and pseudocapacitors (stores energy by fast faradaic redox reaction between electrolyte ions and electrode). Pseudocapacitors possess excellent specific capacitance and higher energy density than EDLC [2,3]. Different metal oxide nanomaterials and conducting polymers have been reported as pseudocapacitive electrode materials as well as for degradation of organic pollutants [2,4,5]. Moreover, the catalytic performance of metal oxide can be controlled using an appropriate synthesis method, compositions, and shapes.
Most transition metal oxides have excellent reversible redox reaction. Among these, TiO$_2$ has received tremendous attention in the last few decades because of its nontoxic properties and excellent optical, photocatalytic, and electrical properties [6]. However, its wide band gap and high resistivity limit wide application in photochemical applications under visible light irradiation, restricting it to use of only 5% of solar light [7]. Additionally, the rapid recombination of electron and hole pairs allows it to respond only to ultraviolet light. In recent years, much attention has been paid to improving the photolytic and electrochemical performance of TiO$_2$, including transition metal doping, surface sensitization, coupling with semiconductor with a narrow band gap, and incorporation with other conducting materials. Doping of TiO$_2$ with transition metal can be a promising way to improve the electric and photocatalytic properties and increase its sensitivity in the visible region due to red shift [8,9]. Transition metals such as Cd, V, Mn, Cr, Zn, Co, and Mo have been reported for doping of TiO$_2$ [10–12]. The use of manganese as a dopant is crucial because it alters the intrinsic optoelectronic properties and can effectively reduce the wide band gap of TiO$_2$ through the creation of defect sites on d-band states [8]. Furthermore, the metallic element can facilitate active centers to trap electrons and holes and reduce electron hole recombination rates [13]. By contrast, as the size of Mn$^{4+}$ is equal to that of Ti$^{4+}$, manganese ions can easily be incorporated into a TiO$_2$ lattice with fewer defect sites and better charge mobility. These changes further improve absorption of visible light and lead to better optical and catalytic properties due to high oxygen mobility [14]. Conductive polymer has been widely used in photolytic devices and supercapacitors. Transition metal oxide offers good specific capacitance and high specific energy, whereas conductive polymer has good intrinsic conductivity; their combined use is a possible candidate for high-performance supercapacitor [15]. Conducting polymer also exhibits fair conductivity in the doping state and lower band gaps compared to conventional polymers. A typical conducting polymer, polyaniline, has received great attention due to its unique optical and tunable electrical conductivities, excellent photoelectronic properties, large surface area, environment stability, good biocompatibility, and environmental friendliness owing to its fused aromatic molecular structures [6,16,17]. It has also been reported to improve the performance of electrode materials for supercapacitor application when combined with a conductive polymer in turn the stability of the composite [6].

In the present study, solvothermally synthesized, Mn-doped TiO$_2$ was decorated with a polyaniline membrane by oxidative polymerization of aniline. To the best of our knowledge, PANi/Mn-TiO$_2$ composite has not been presented as a bifunctional supercapacitor and photocatalytic material. Photocatalytic degradation of methylene blue and electrochemical performance of this doped TiO$_2$ was investigated, illustrating a decrease in band gap to 1.9 eV. Subsequently, X-ray diffraction spectroscopy (XRD), Fourier-transform infrared spectroscopy (FTIR), high-resolution transmission electron microscopy (HRTEM), and UV-visible spectroscopy were used to analyze the physiochemical properties. The as-prepared composite is used as electrode material for three-electrode and two-electrode cell setups. The electrochemical measurements demonstrate a specific capacitance of 635.87 F g$^{-1}$ of the synthesized composites at a current density of 1 A g$^{-1}$, which is almost four times that of bare TiO$_2$. The photodegradation of methylene blue was also investigated. The synthesized PANi/Mn-TiO$_2$ nanocomposite is expected to show high absorbance in visible light. This study is intended to provide inspiration to determine a pathway for enhancing electrochemical and photocatalytic performance of TiO$_2$.

2. Results and discussion

2.1. Physiochemical and Morphological Characterization

Figure 1a displays the XRD patterns of different samples. Diffraction peaks at 25.39°, 37.89°, 48.05°, 54.00°, 55.17°, 62.69°, 68.94°, 70.44°, and 75.19° observed in XRD patterns of TiO$_2$ nanoparticles correspond to (101), (004), (200), (105), (211), (204), (116), (220), and (215) and were well matched with those of tetragonal anatase TiO$_2$ (JCPDS card no 01-072-1147) [18,19]. The XRD patterns of Mn-TiO$_2$
show a decrease in peak intensities with no additional peak related to manganese oxide. The decrease in intensities of Mn-doped TiO$_2$ is attributed to loss of crystallinity caused by lattice distortion of Mn doping originating from 3d and 4s orbitals of Mn below the conduction band of TiO$_2$ [20]. However, the peaks of manganese were not detected in Mn-TiO$_2$ possibly due to relatively low concentration of manganese doping [21]. Moreover, in the XRD spectra of PANi/Mn-TiO$_2$, the additional characteristic peaks of polyaniline at 22° to 27° indicate the presence of polyaniline in the composite, while (200) and (204) plane suggests the exitance of TiO$_2$ [22]. When the PANi is deposited on the surface of Mn-TiO$_2$ particle, the diffraction peak of both pure PANi and Mn-TiO$_2$ decreases significantly, revealing the poor crystallinity of the prepared composites.

The FTIR result of PANi/Mn-TiO$_2$ is shown in Figure 1b, with the characteristic bands at 1583.6 cm$^{-1}$ and 1494.79 cm$^{-1}$ attributed to C=C stretching modes of quinoid and benzenoid units of polyaniline, respectively [23]. Similarly, the peaks around 1148 cm$^{-1}$ are characteristic for degree of delocalization and correspond to conductive polyaniline [24]. The bands from 400 cm$^{-1}$ to 700 cm$^{-1}$ represent various stretching and bending modes of Ti–O–Ti, indicating the presence of TiO$_2$ nanoparticles in the composite, as are indexed in FTIR spectra of TiO$_2$ and Mn-TiO$_2$ [25]. Moreover, the wavenumber shifts slightly higher for Mn-TiO$_2$ than for pure TiO$_2$. Consequently, the broad peaks around 3200 cm$^{-1}$ to 3400 cm$^{-1}$ are due to stretching vibrations of O–H groups of water molecules present in all samples of TiO$_2$, Mn-TiO$_2$, and PANi/Mn-TiO$_2$ [13]. The above results demonstrate successful formation of PANi/Mn-doped TiO$_2$.

![Figure 1. (a) XRD plots of TiO$_2$, Mn-TiO$_2$ and PANi/Mn-TiO$_2$ nanoparticles (inset shows the magnified diffraction patterns within 20 = 45° to 65°), and (b) FTIR spectra of TiO$_2$, Mn-TiO$_2$ and PANi/Mn-TiO$_2$ nanoparticles.](image)

TEM was used to characterize the morphology and size of TiO$_2$, Mn-TiO$_2$, and PANi/Mn-TiO$_2$. Figure 2a–d shows the HRTEM of TiO$_2$, Mn-TiO$_2$, and PANi/Mn-TiO$_2$. The average size of the nanoparticles is 40–50 nm, determined by Scherrer equation with the help of XRD spectra. The interspacing distance of 0.324 nm in Mn-doped TiO$_2$ corresponds to the (101) crystal plane, whereas the blurred lattice fringes in the HRTEM image of Mn-doped TiO$_2$ revealed the covering membrane of polyaniline. The increase in nanoparticle size in addition to PANi indicates successful formation of PANi membrane on the Mn-TiO$_2$ nanoparticles [19]. Likewise, the FE-SEM image of PANi/Mn-TiO$_2$ (Figure S1 and its inset) clearly shows homogenous wrapping of the polyaniline membrane over the Mn-TiO$_2$ surface. The EDS revealed peaks of C, N, Mn, Ti, and O, confirming the presence of elements in PANi/Mn-TiO$_2$. In addition, TiO$_2$ acts as the template for uniform polymerization of aniline, and such morphology is propitious to increase the active contact area for electrolyte ions and eventually leads to better electrochemical activity. Meanwhile, the outer PANi layer could protect TiO$_2$ from reductive dissolution, resulting in good enhanced electrochemical and photolytic stability [26,27].
Figure 2. Morphological analysis, HRTEM image of (a) TiO$_2$, (b) Mn-TiO$_2$, (c,d) PANi/Mn-TiO$_2$ nanoparticles.

Figure 3a represents the UV-Visible absorption spectra of TiO$_2$, Mn-TiO$_2$, and PANi/Mn-TiO$_2$. The broad, high-intensity adsorption bands at ~315 nm can be ascribed to $\pi-\pi$ transition of benzenoid rings (fully reduced form) of PANi [28]. The UV-Vis results are consistent with FTIR studies. The increase in adsorption capacity is related to structural modification, which is attributed to insertion of Mn cations and good interaction between PANi and anatase TiO$_2$. To further study the photocatalytic effect of the composites, a Tauc plot was derived from the UV-Vis spectrum (Figure 3b). The increase in adsorption intensity after the incorporation of PANi and Mn in PANi/Mn-TiO$_2$ can be attributed to the visible light activity of TiO$_2$ and Mn-TiO$_2$ [29,30]. Furthermore, the adsorption spectra show that TiO$_2$ does not show any absorbance in the visible region. The absorbance increases after doping with Mn to produce Mn-TiO$_2$ and shows an uptrend in PANi/Mn-TiO$_2$, accounting for the high photocatalytic activity in visible light region. The band gap energy for PANi/Mn-TiO$_2$ remains at 1.9 eV, which is very low compared to those of Mn-TiO$_2$ (3.0 eV) and TiO$_2$ (3.4 eV), which is more narrow than the previously reported TiO$_2$-based composites. The narrow band gap results indicate coordination of TiO$_2$ with nitrogen atom and possible $\pi-\pi$ interaction between Mn and the PANi-conjugated system. Additionally, the narrow band gap might be attributed to wrapping of PANi on the Mn-TiO$_2$ surface or
due to proper interaction of the components of the system. The sub band states and Mn⁺ and oxygen defects are responsible for the reduction of bandgap of TiO₂ [31].

![Figure 3. (a) UV-Visible spectra, and (b) Tauc plot of TiO₂, Mn-TiO₂ and PANi/Mn-TiO₂ nanoparticles.](image)

2.2. Electrochemical Performance

The electrochemical performance of TiO₂, Mn-TiO₂ and PANi/Mn-TiO₂ was investigated by CV measurements in a potential window of 0 to 0.6 V at different scan rates of 5 mVs⁻¹ to 100 mVs⁻¹ in a standard three-electrode configuration. Figure 4a shows the CV curves of Ni foam, TiO₂, Mn-TiO₂, PANi/Mn-TiO₂, and pure PANi at the scan rates of 5 mV s⁻¹. CV curves of Ni foam do not contain any distinct redox peak, suggesting no significant contribution to capacitance of the electrode material. The CV curve indicates that the capacitance characteristics are mainly governed by faradaic reactions, different from that of electric double layer capacitors (EDLC). The characteristic current response of TiO₂ is related to the Ti⁴⁺/Ti³⁺ transformation, and the reverse intercalation and deintercalation of K⁺ ion. All the electrodes display a quasi-rectangular CV profile, indicating excellent faradaic reaction, and electrolytes reveal excellent pseudocapacitive properties, which can be distinguished from the existence of a pair of oxidation and reduction peaks. Our results indicate that CV area increases from TiO₂ electrodes to Mn-TiO₂ and PANi/Mn-TiO₂ electrodes, resulting in significant increase in specific capacitance of the composites. In addition, anodic and cathodic peak separation was much smaller for PANi/Mn-TiO₂ and is ascribed to fast kinetic reversibility, ensuring the high capacity of PANi/Mn-TiO₂. A sharp peak at the end of the CV curve was observed above 0.5 V, indicating the evolution of a of oxygen during the electrochemical test, which is due to higher applied potential voltage [32]. The peak current increases with increasing scan rate, but the anodic to cathodic peak current ratio remains nearly constant (Figure 4b). The pair of redox peaks remains at 100 mVs⁻¹, suggesting excellent intercalation and deintercalation of electrolyte ions at higher scan rates. The oxidation and reduction peaks shift to positive and negative potential, mainly attributed to limited diffusion and migration of electrolyte ions at the electrode surface. To elucidate the charge transfer mechanism, a linear variation between redox peak current versus square root of scan rates demonstrates the diffusion-controlled reversible redox reaction on the surface of PANi/Mn-TiO₂ composites (Figure S2) [33]. With the insertion of Mn dopants, because of the formation of Ti-O-Mn in response to the Ti⁴⁺ is replaced by the Mn⁴⁺ that is compensated by forming an oxygen vacancy. Figure 4c presents 30 consecutive CV cycles of PANi/Mn-TiO₂ at a scan rate of 150 mVs⁻¹, where minimal lap displacement was observed, indicating excellent long-term electrochemical stability of PANi/Mn-TiO₂.
Galvanostatic charge discharge (GCD) measurements were performed to understand the capability of the prepared electrode at the potential range of 0 to 0.45 V and current densities from 1 A g\(^{-1}\) to 5 A g\(^{-1}\). The GCD curves shown in Figure 4d show the symmetrical triangular charge-discharge curve, representing good pseudocapacitive performance, as seen in CV measurements. The specific capacitance of the as-prepared electrode was calculated to be 635.87 F g\(^{-1}\) at 1 A g\(^{-1}\), which is greater than those of Mn-TiO\(_2\) (326.69 F g\(^{-1}\)), TiO\(_2\) (162.22 F g\(^{-1}\)), and PANi (135.55 F g\(^{-1}\)) at the same current density. In Figure 4e, GCD curves of PANi/Mn-TiO\(_2\) at different current densities are plotted, showing that an increase in current density decreases the discharge time. This occurs because, at higher current density, the electrolyte ions do not penetrate deep into the bulk of the electrode and hence take less time for charging and discharging processes. Moreover, the specific capacitance was 595.65 F g\(^{-1}\), 544.23 F g\(^{-1}\), 462.29 F g\(^{-1}\), and 408.53 F g\(^{-1}\) at current densities of 2 A g\(^{-1}\), 3A g\(^{-1}\), 4 A g\(^{-1}\), and 5A g\(^{-1}\), respectively. The specific capacitance as calculated from GCD curves is plotted in Figure 4f, showing that the PANi/Mn-TiO\(_2\) electrode produces higher specific capacitance at the same current density. The remarkable enhancement of capacitance is attributed to well-developed synergy between components of the active electrode materials. The specific capacitance of the PANi/Mn-TiO\(_2\) remains at 64.25% of its initial capacitance at a high current density of 5 A g\(^{-1}\). The specific capacitance of Mn-doped TiO\(_2\) also improved by two times compared to that of pure TiO\(_2\), but the obtained value is less than that of PANi-Mn-TiO\(_2\). Among the three-electrode material, the best capacitance of the final composite is due to its narrower band gap. A low band gap energy fosters better charge transport, leading to the better supercapacitive performance. The high specific capacitance of the composite is attributed to the stable conducting polymer (PANi) serving as a binder to all components and prevents dissolution of TiO\(_2\) in electrolytes. To understand the charge transfer resistance of the electrode, electrochemical impedance spectroscopy was performed in the frequency range of 0.01 to 1000 kHz at 10 V bias potential, and corresponding Nyquist plots are compared. As shown in Figure 5a, the Nyquist curve consisted of a semicircular section at the higher frequency region, which is related to charge transfer.
resistance and the linear section at lower frequency region revenant to Warburg resistance. Moreover, the PANi/Mn-TiO₂ shows the smallest semicircle radius in the high-frequency region and a line nearly perpendicular to the X-axis (Z’ real) in the low-frequency region; the results reflect a comprehensive outcome of easier ion diffusion and low internal resistance. Life cycle stability is another important factor for determining the suitability of electrode materials. The cycling stability of PANi/MN-TiO₂ was tested by a GCD charge-discharge curve at 10 A g⁻¹ over 5000 cycles (Figure 5b). The PANi/Mn-TiO₂ retained excellent stability of 91% of its initial capacitance. The excellent electrochemical properties of the PANi/Mn-TiO₂ composite electrode allow proper synergy of each component, a larger number of vacant sites in TiO₂ due to Mn doping, and a narrower band after conductive polymer coating [18,34]. A comparison of the electrochemical performance of TiO₂-based composites elucidates the significance of this work (Table S1). It is evident that the material synthesized in our work compares well with previous work and performs better than many of them, showing its suitability as a good supercapacitor electrode material.

![Nyquist plots](image)

**Figure 5.** EIS and stability test, (a) Nyquist plots of TiO₂, Mn-TiO₂ and PANi/Mn-TiO₂, and (b) cycling stability of PANi/Mn-TiO₂. (Inset (b) shows GCD profile before and after cyclic stability test).

### 2.3. Asymmetric Supercapacitor

To evaluate the potential of this PANi/Mn-TiO₂ super capacitor, a fully assembled asymmetric supercapacitor (PANI/Mn-TiO₂/AC) was fabricated. Before device fabrication, PANi/Mn-TiO₂ and activated carbon were coated on the surface of nickel foam as positive and negative electrodes, respectively, after Whatman filter paper separation as shown in Figure 6a. The negative electrode was also electrochemically characterized by CV and GCD measurements in the potential window of −1.0 V to 0 V. The specific capacity of the negative electrode was calculated from GCD curves (Figure S3). To maintain the charge balance, the mass ratio of negative and positive electrodes for an asymmetric supercapacitor was calculated using equation [35]:

\[
\frac{m^+}{m^-} = \frac{C^- \times V^-}{C^+ \times V^+}
\]

where m⁻, C⁻, and V⁻ are the mass, specific capacitance, and potential window of the negative electrode, respectively, and m⁺, C⁺, and V⁺ are the mass, specific capacitance, and potential window of the positive electrode.

Figure 6b represents the CV curve of negative and positive electrodes at the scan rate of 5 mV s⁻¹, −1.0 to 0 V and 0 to 0.6 V versus Ag/AgCl reference electrode, respectively. The almost rectangular CV curve of AC indicates the ELDC behavior, and the CV profiles of PANi/Mn-TiO₂ suggest its pseudocapacitive behavior. The cell potential used for PANi/Mn-TiO₂ was 0–1.6 V. In the potential
range of 0–1.6 V, stable cyclic voltammogram was observed. The CV profiles of PANi/Mn-TiO$_2$//AC at different scan rates are shown in Figure 6c, which indicates no change in the shape of the CV curve, suggesting the good reversibility and high rate capability of the PANi/Mn-TiO$_2$//AC supercapacitor device. The GCD profile (Figure 6d) of this supercapacitor device was tested at different current densities of 1 A g$^{-1}$ to 5 A g$^{-1}$ in a potential window of 0 to 1.6 V. This profile portrays a symmetric nature at high potential, indicating excellent capacitance properties, redox reversibility, and high efficiency. The change in charge discharge time with increasing current density is clear. The specific capacitance decreases from 52.5 F g$^{-1}$ to 16.56 F g$^{-1}$ when the current density increases from 1 A g$^{-1}$ to 5 A g$^{-1}$. The cyclic stability of this device was tested by continuous GCD cycles at 5 A g$^{-1}$ for 5000 cycles in a voltage range of 0 V to 1.6 V (Figure 6e). The PANi/Mn-TiO$_2$//AC attains superior life cycle stability of 89%, indicating excellent cyclic stability of the PANi/Mn-TiO$_2$ nanocomposite electrode materials. In Figure 6f, the Ragone plot of the asymmetric PANi/Mn-TiO$_2$ cell shows excellent cell performance. This asymmetric PANi/Mn-TiO$_2$//AC device attains 18.66 W h Kg$^{-1}$ at a power density of 800 W kg$^{-1}$.

Figure 6. Asymmetric supercapacitor device performance, (a) schematic representation of assembled asymmetric device, (b) CV plot of AC and PANi/Mn-TiO$_2$ at 5 mV s$^{-1}$, (c) CV curve of asymmetric device at different scan rates, (d) charge discharge profiles of asymmetric device at various current densities, (e) life cycle stability of asymmetric device at 10 A g$^{-1}$ (inset shows few final charge discharge cycle), (f) Ragone plots.

2.4. Photocatalytic Effect of PANi/Mn-TiO$_2$ for Degradation of Methylene Blue

The photocatalytic activity of pure TiO$_2$, Mn-TiO$_2$, and PANi/Mn-TiO$_2$ was tested by analyzing the photodegradation of methylene blue (MB) in aqueous solution under visible light irradiation. For degradation, 30 mL of 10 ppm MB solution was added to a beaker containing 0.025 gm catalyst and kept in a dark room for 30 min. MB is a typical synthetic dye, used extensively for fabric dyeing, which has several health risks. So, MB was selected for degradation. A 300 W Xe lamp with UV and IR filters was used as a light source with photon wavelength 150 nm. The irradiation energy was calculated by the following equation [36]:

$$E = \frac{h \times c}{\lambda}$$  \hspace{1cm} (2)
where, h, c and λ are planks constant \((4.136 \times 10^{-15} \text{ eV s})\), speed of light \((2.998 \times 10^{17} \text{ nm s}^{-1})\), and wavelength (nm) respectively.

The reaction was followed by UV-Visible spectroscopy in a 3 min time interval (Figure 7a). As can be seen in Figure S4, ~89 % removal of MB solution took place after 24 min and ~98% within 27 min, which is superior among recently reported TiO\(_2\)-based photocatalytic materials (Table S2). However, only 50% removal took place when pure TiO\(_2\) was used and that increases to 66% after using Mn-TiO\(_2\). The result shows the shortest photocatalyst degradation time. The PANi/Mn-TiO\(_2\) composites exhibited remarkably higher catalytic activity, suggesting that the activity of TiO\(_2\) is improved by doping with manganese and incorporation of PANi membrane (Figure 7b). Figure 7c shows that the degradation reaction of MB followed by the Langmuir–Hinshelwood kinetic relation [30]:

\[
\ln \frac{C}{C_0} = kt
\]  

where \(k\) (min\(^{-1}\)) is the rate constant, \(t\) (min) is the time, and \(C\) and \(C_0\) are the initial and final MB concentration.

Figure 7. Photocatalytic activity, (a) absorbance spectra of the MB by PANi/Mn-TiO\(_2\), (b) degradation of MB by different samples, (c) kinetic curves of studied photocatalyst, (d) schematic illustration of photocatalysis mechanism of PANi/Mn-TiO\(_2\) composite catalyst for MB degradation under visible light irradiation.
MB removal efficiency for TiO$_2$, Mn-TiO$_2$, and PANi/Mn-TiO$_2$ were calculated using Equation (4):

$$\text{MB removal efficiency (\%) } = \frac{(C - C_0)}{C} \times 100$$  \hspace{1cm} (4)

The enhancement of photocatalytic properties of PANi/Mn-TiO$_2$ may be the result of a suitable ratio of components in the composite, increasing the total number of active sites in PANi/Mn-TiO$_2$ available for photocatalytic reaction and to hinder rapid recombination of electron and hole (e$^-$/h$^+$) pairs [29]. Moreover, PANi acts as the photosensitizer in PANi/Mn-TiO$_2$ to sensitize the TiO$_2$ surface. Due to the inactivity of TiO$_2$ in the visible light region, pure TiO$_2$ has very poor photolytic activity. Figure 7d representation for the photocatalytic mechanism of PANi/Mn-TiO$_2$. The enhanced activity of Mn doping is due to its half-filled electronic structure, which can act as active trap sites to accelerate the charge transfer processes. This process may promote the generation of superoxide and hydroxyl radicals, which results in reduction of the (e$^-$/h$^+$) pair recombination, resulting in better photolytic activities in the visible light region compared to pure TiO$_2$. On the other hand, PANi membrane on the surface of TiO$_2$ nanoparticles easily drives the photogenerated electron, creating a strong oxidative/reductive state of oxide nanoparticles, thus, the photogenerated holes in PANi may be trapped within the TiO$_2$ nanoparticles enhancing the oxidative properties of TiO$_2$ [37].

3. Materials and Methods

3.1. Materials and Reagents

All the chemicals were analytical grade and used as received. Titanium tetraisopropoxide (TTIP), triethanolamine (TEOA), diethylamine, polyvinylidene fluoride (PVDF), aniline hydrochloride, activated carbon (AC), and N-methyl-2-pyrrolidene (NMP) were obtained from Sigma Aldrich (St. Louis, MO, USA). Manganese sulfate monohydrate (MnSO$_4$·H$_2$O), methylene blue trihydrate (MB), absolute ethanol, and ammonium persulfate were purchased from Samchun Chemicals (Gyeonggi-Do, South Korea). Nickel foam was obtained from Goodfellow Cambridge Limited (Huntingdon, England). Ultra-pure distilled (DI) water was used throughout the work.

3.2. Synthesis of Mn-TiO$_2$

Mn-doped TiO$_2$ was synthesized by solvothermal treatment of 2 mmol titanium tetraisopropoxide (TTIP) and 1 mmol triethanolamine (TEOA) in 20 mL absolute ethanol. Next, 0.1 mmol MnSO$_4$·H$_2$O was added to the above solution and kept under constant magnetic stirring for 1 h. A solution of 50 mL absolute ethanol, 1 mL diethylamine, and 25 mL water was mixed in and stirred for 6 h. The resulting solution was transferred to a Teflon-lined autoclave and heated at 200 °C for 12 h. The solid product was washed with DI water and ethanol several times and eventually dried overnight at 80 °C. Pure TiO$_2$ was prepared by the same process without addition of MnSO$_4$·H$_2$O.

3.3. Preparation of PANi/Mn-TiO$_2$

For preparation of PANi/Mn-TiO$_2$, firstly 0.1 gm Mn-doped TiO$_2$ was dispersed in 30 mL HCl (0.02 M) and sonicated for 30 min. Acidic solution (10 mL 0.02 M HCl) of aniline (0.1 mL) was added to the previous dispersion, followed by 0.25 gm of ammonium persulfate. This final solution was stirred in ice for 1 h. Finally, the precipitate was centrifuged and washed with DI water/ethanol several times and eventually dried overnight at 80 °C. Pure PANi was prepared by employing the same procedure without using Mn-TiO$_2$.

3.4. Characterization Techniques

A wide-angle X-ray diffractometer (XRD, Rigaku Co., Akishima, Japan, cu k Cu Kα with $\lambda = 1.540$ Å) was used to analyze crystallinity of the samples. Fourier transform infrared spectroscopy (FTIR, ABB Bomen MB 100 spectrometer, Bomen, QC, Canada) was used with KBr pellets within the
wavenumber range of 400 cm\(^{-1}\) to 4000 cm\(^{-1}\). Transmission electron microscopy (TEM, equipped with JEM-2200, JEOL, Tokyo, Japan) was used to study the morphology of particles. The adsorption spectra were observed by UV-visible spectrometer (Lambda 900, Perkin Elmer, Shelton, CT, USA).

3.5. Electrochemical Measurements

All the electrochemical measurements of cyclic voltammetry (CV), galvanostatic charge discharge (GCD), and electrochemical impedance spectroscopy (EIS) of the prepared composite were analyzed by ZIVE SP2 electrochemical workstation (GyeonGi-Do, South Korea) at room temperature by two-electrode and three-electrode cell setups. For preparation of the PANi/Mn-TiO\(_2\) nanocomposite as a working electrode, 4 mg of the nanocomposite was mixed with 0.5 mg of carbon black and 0.5 mg of PVDF. A slurry of the mixture was prepared by adding excess NMP solution, and the prepared solution was cast in Ni-foam (1 cm \(\times\) 1 cm). The electrochemical activities were measured by a three-electrode cell setup in 2 M KOH solution as electrolyte using Ag/AgCl as the reference electrode and platinum wire as the counter electrode within the potential range of 0 to 0.6 V.

Specific capacitance of the electrode was determined by CV using the following relation [38]:

\[
\text{Specific capacitance (}\ C_{sp}\text{)} = \frac{\int IV}{2mV}
\]

The specific capacitance was estimated with the GCD test according to the following equation [39,40]:

\[
\text{Specific capacitance (}\ C_{sp}\text{)} = \frac{I \times t}{V \times m}
\]

where \(C_{sp}\), \(\Delta t\), \(\Delta V\), and \(m\) are the specific capacitance, discharge time, potential window, and active mass of the electrode, respectively.

The energy and power density were calculated using the following relationships [41,42]:

\[
\text{Energy density (}\ E\text{)} = \frac{C_{sp} \times (\Delta V)^2}{7.2}
\]

\[
\text{Power density (}\ P\text{)} = \frac{E \times 3600}{\Delta t}
\]

Here, \(V\) is the potential window, and \(t\) is the discharge time.

4. Conclusions

In summary, we reported bifunctional PANi/Mn-TiO\(_2\) nanoparticles produced by sol gel-assisted solvothermal reaction followed by oxidative polymerization. The structural and physiochemical properties of the composite were analyzed using XRD, FTIR, HRTEM, and UV visible spectra and confirmed successful synthesis of the composites. The electrochemical and photochemical characteristics of TiO\(_2\), Mn-TiO\(_2\), and PANi/Mn-TiO\(_2\) samples were investigated. The highest specific capacitance was observed for PANi/Mn-TiO\(_2\) (635.87 F g\(^{-1}\) at 1 A g\(^{-1}\)) composite compared to all other electrodes prepared in this work. Further, an asymmetric supercapacitor assembled using PANi/Mn-TiO\(_2\) and activated carbon (AC) delivered an energy density of 18.66 Wh kg\(^{-1}\) at a power density of 800 W kg\(^{-1}\) and 89% capacity retention after 5000 charge-discharge cycles. In addition, all the samples were used for degradation of methylene blue, and the PANi/Mn-TiO\(_2\) showed excellent degradation in a very short time. The presence of manganese ions and a PANi layer produced a gradual decrease in band gap energy. It is expected that this work could promote bifunctional efficiency of TiO\(_2\)-based composites as a practical supercapacitor and photocatalytic materials.
Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/5/546/s1, Figure S1: FESEM image of PANi/Mn-TiO$_2$ (inset shows the EDS profile), Figure S2: Peak current versus square root of scan rates, Figure S3: GCD curves of activated carbon at different scan rates, Figure S4: Photocatalytic reduction of MB for TiO$_2$, Mn-TiO$_2$ and PANi/Mn-TiO$_2$, Table S1: Comparative study of electrochemical performance of TiO$_2$ based nanocomposites, Table S2: Comparative study of photocatalytic performance of TiO$_2$ based nanocomposites.

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