TiO$_X$-polyaniline Composite Films for High-performance Supercapacitors

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TiO$_X$-polyaniline (PANI) nano-composite thin films are synthesized using an electrochemical deposition technique for supercapacitor applications. The PANI-TiO$_X$ composite films show granular porous morphologies along with PANI nanofibers. The electrochemical supercapacitor properties of the PANI and the composite PANI-TiO$_X$ films are examined in a 0.5-M LiClO$_4$ electrolyte. The pure PANI film shows a comparatively higher specific capacitance whereas the PANI-TiO$_X$ composite films are more stable with high power and energy densities. Negligible capacitance loss is obtained for the PANI-TiO$_X$ composite films over 1000 charge-discharge cycles. The composite films show considerably improved power-density and energy-density values of $\sim$31.2 kW/kg and $\sim$35.2 Wh/kg, respectively.

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Recently, because the portable electronic device market has been growing rapidly, supercapacitors are expected to play an important role in power-source applications and have received considerable attention [1–4]. A supercapacitor is a new kind of energy storage device that possesses the properties of an ordinary capacitor and battery, but exhibits a 20-200 times larger capacitance per unit volume or mass than conventional capacitors. Among various supercapacitor electrode materials, polyaniline (PANI) is one of the most promising due to its high electronic conductivity, good solubility in various solutions, simple synthesis process, and environmental stability [5–8]. PANI is typically prepared by chemical [5–7, 9] or electrochemical oxidation [10–13] of aniline, but electrochemical deposition is a facile way for synthesizing a large-area film [14]. Because PANI has three different oxidation states, doping PANI is related to the control of its redox states [6, 7].

Since electrochemical doping of PANI is regarded as electrochemical oxidation or reduction [10], composites consisting of PANI and various materials such as graphene, Ru, Au, Ag, CNT have been widely studied for supercapacitor applications [15–19]. Specific capacitances of 474 F/g and 569 F/g were obtained for PANI/RuO$_2$ and graphene/PANI/CNT films, respectively [16, 19]. Despite a considerable effort to develop PANI and various doping materials for supercapacitor applications, studies on the power and the energy densities have been rarely conducted. Recently, the power and the energy densities have been noticed to be key factors that must be considered for applications replacing conventional batteries [20].

In this work, we propose a way to improve the power and the energy densities of PANI-based supercapacitors by using titanium oxide (TiO$_X$) as an electrode template. The fabrication of PANI-TiO$_X$ composite films is accomplished by using electrochemical polymerization. The charge-discharge performance and the impedance spectra show that both the power and the energy densities of the PANI-TiO$_X$-based supercapacitors are improved. PANI-TiO$_X$ composite thin films were synthesized on ITO (25–27 $\Omega$/cm$^2$)-coated conducting glass substrates by using an electro-deposition technique. Prior to the deposition, the ITO substrate were cleaned consecutively in acetone, methanol, and deionized water (18.2 MΩcm). The chemicals, such as aniline, H$_2$SO$_4$ (98%), and titanium (IV) oxyacetylacetonate (Ti oxyAC, 90%), and all other reagents were used as received without further purification. The electro-polymerization was carried out in a one-compartment cell by using a three-electrode system in which ITO was the working electrode, graphite the counter electrode, and a saturated calomel electrode (SCE) the reference electrode. Solutions of 0.2-M aniline and 0.5-M H$_2$SO$_4$ were prepared in an aqueous medium by using DI water. The mixture was sonicated for 20 min to initiate the polymerization process. TiO$_X$ solutions were prepared in methanol by changing the mole percent of Ti oxyAC per mole percent of aniline monomer. The chemical reaction is given below:

$$TiC_{10}H_{14}O_5 + CH_3OH \rightarrow TiO_2 + 11CO + 9H_2O \uparrow \tag{1}$$

In Eq (1), we can notice that Ti oxyAC reacts with
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Fig. 1. (Color online) SEM images of PANI and PANI-TiO$_X$ composite films: (a) PANI, (b) PANI-Ti10, and (c) PANI-Ti20. Cyclic voltammograms at different scan rates of 20, 50, 80 and 100 mV/s for (d) PANI, (e) PANI-Ti10, and (f) PANI-Ti20.

methanol and creates TiO$_X$ at room temperature [21]. The pure PANI and the PANI-TiO$_X$ composite films were electrodeposited potentiostatically at 0.8 V (versus SCE) for 30 min by using Princeton-Applied-Research-made VersaSTAT3 potentiostat. The pure PANI and the composite films were denoted as PANI, PANI-Ti10 and PANI-Ti20, respectively. Ti10 and Ti20 indicate that the Ti mole percentages are 10% and 20%, respectively. A potentiostat/glavanostat was used in the galvanostatic mode to record the charging and discharging characteristics of the supercapacitor electrode films. The electrochemical impedance spectroscopy (EIS) measurement was performed in the AC frequency range from 1 MHz to 1 Hz by using an impedance analyzer.

Figures 1(a)-(c) show the SEM images of the PANI, PANI-Ti10, and PANI-Ti20 films, respectively. The PANI film shows a nano-fibrous morphology (Fig. 1(a)) whereas the PANI-Ti10 (Fig. 1(b)) and the PANI-Ti20 (Fig. 1(c)) films show spherical aggregations of TiO$_X$ on the PANI nanofibers. The PANI nanofibers have a length of about 700 nm while the PANI-TiO$_X$ composite has a granular shape with a length of about 800 nm $\sim$ 1.1 $\mu$m. For a higher concentration of the Ti oxyAC solution in the precursor PANI solution, an increased aggregation of TiO$_X$ is observed, possibly due to the formation of more templates for PANI nucleation. The oxidation process is become to be strongly affected by the nucleation of PANI, leading to aniline agglomeration [22]. PANI polymerization occurs on the surface of TiO$_X$ because TiO$_X$ is a strong oxidant having many vacancies on its surface [6]. The obtained TiO$_X$ values are considerably lower than they are for the addition of Ti oxyAC, which is presumably because aniline is polymerized electro-conductive polyaniline around the TiO$_X$ while Ti oxyAC produces a nonconductive TiO$_X$.

The electrochemical supercapacitor properties of the films were determined using cyclic voltammetry. Figures 1(d)-(f) show the cyclic voltammograms (CV) curves for the films at different scan rates in a PC (propylene carbonate, 99%) electrolyte containing 0.5-M LiClO$_4$. The CV curves were cycled between 1.0 V (versus SCE) and 0.2 V (versus SCE) potential windows. The rectangular shape of these CVs at a 20 mV/s scan rate indicates the ideal pseudo-capacitive behavior of the electrodes. However, with increasing scan rate, Li$^+$ ions diffuse on the surface of the electrode, resulting in a deviation from the ideal CV shape. The specific capacitance ($C_S$) of the electrode can be calculated from the CV curves according to the following equation:

$$C_S = \frac{i}{r \times m}, \quad (2)$$