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Effects of TiO_2 Nanoparticle Doping in Coconut-shell Carbon on the Properties of Supercapacitor

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In this study, TiO_2 nanoparticles at different weight ratios were added to composite coconut-shell carbon and conductive carbon black electrode material to investigate their effects on the properties of a supercapacitor. Then, the composite carbon electrodes were further treated by rapid thermal annealing (RTA) and measured by field emission scanning electron microscopy (FE-SEM), electronic data system (EDS) analysis, cyclic voltammetry (CV), and charge–discharge and photoluminescence (PL) tests to investigate the diverse effects on the electrodes with conductive carbon black doped with TiO_2 nanoparticles and on the electrodes treated with and without RTA. According to the results of CV, the capacitance of electrodes without TiO_2 nanoparticles was determined to be 73.104 F/g by scanning at a rate of 25 mV/s, and could be increased to 96.54 F/g with TiO_2-doped carbon electrodes. In addition, the capacitance of carbon electrodes with TiO_2 could be increased to 171.28 F/g after heat treatment by RTA.

1. Introduction

The car industry has developed over a period of one hundred years, but the consumption of energy and air pollution generated by cars have caused an energy crisis and global warming. Recently, it has been observed that the developed cars tends to have increaseed energy efficiency and reduced pollution output. In line with those developments, all the research and attention has turned to electric cars in every country. A supercapacitor is suitable for increasing the power and energy storage capacity of electric cars. Therefore, the supercapacitor will be a key element of electric cars in the future. The supercapacitor is an electrochemical device that stores energy via polarized electrolytes. It is different from a traditional chemical electric power storage device because the energy storage depends on the electric double layer, redox pseudocapacitance, and charge. This electric power storage device has a special function compared with traditional capacitors and batteries. It does not induce any chemical reaction

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during the energy-storing procedure, and the process is reversible. Thus, the supercapacitor can be charged and discharged many times. The principle is the same as those of other electric double-layer capacitors. The supercapacitor has a large capacity resulting from the use of activated carbon porous electrodes and electrolytes. Its characteristics include high energy density, high power density, long lifetime, wide operating temperature range, fast charge and discharge, and long standing time. It is also maintenance-free and environmentally friendly. Activated carbon is a porous electrode carbon, and holes can increase the activated carbon area of the absorbing impurity. The factors that affect the charge storage capability are the specific surface area, pore structure, and type of surfactant.[1–4]

A highly specific surface-area activated carbon has a wide microporous distribution range with an aperture less than 2 mm, and it cannot be efficiently used when the microporous were at high power discharging process. TiO_2 is an n-type semiconductor and an intelligent metal oxide that exhibits chemical stability, physical stability, biological compatibility, high melting point. (rutile: 1855 °C), high band gap (rutile: E_g = 3.0 eV direct band gap; anatase: E_g = 3.2 eV indirect band gap), high refractive index (rutile: 2.609; brookite: 22.583; anatase: 2.488), stable light property, high dielectric constant, and high optic conversion efficiency. In this research, a cheap coconut-shell carbon was used to prepare a supercapacitor with low conductivity. To improve the low conductivity of cheap coconut-shell carbon, TiO_2 and conductive carbon were added to produce composite carbon, which increased the performance of capacitors and electrodes. Indium tin oxide (ITO) conductive glass was applied to the substrate as the collector plate, coated with platinum, and added with conductive carbon to increase conductivity. In this study, TiO_2 nanoparticles were added to composite coconut-shell carbon and conductive carbon black electrode material to investigate their effects on the properties of a supercapacitor.[5–11]

2. Materials and Methods

2.1 Materials

First, different quantities of carbon black and TiO_2 were added to coconut-shell carbon and stirred with a magnet mixer. After baking to produce composite-structure carbon, polyvinyl butyral (PVB) was added to obtain carbon paste. The ITO substrate was coated with this carbon paste by spin coating and then the composite electrode was finished. The previously discussed parameters of TiO_2 were found to provide the best fabrication parameters by physical and electrochemical analyses. Second, annealing and oxygenation at different temperatures were carried out to test the effects on the supercapacitor in the cases with and without annealing. Third, $LiClO_4$ was used to prepare the electrolyte, and the charge–discharge efficiency was considered to discuss the effect on the capacitor of different scanning speeds. Figure 1 shows the flowchart of the sample preparation and analysis.

2.2 Experimental methods

Cyclic voltammetry (CV) was performed to detect the type of current by changing the applied voltage. Each analyte has a different redox potential, and its specific capacitance was calculated using

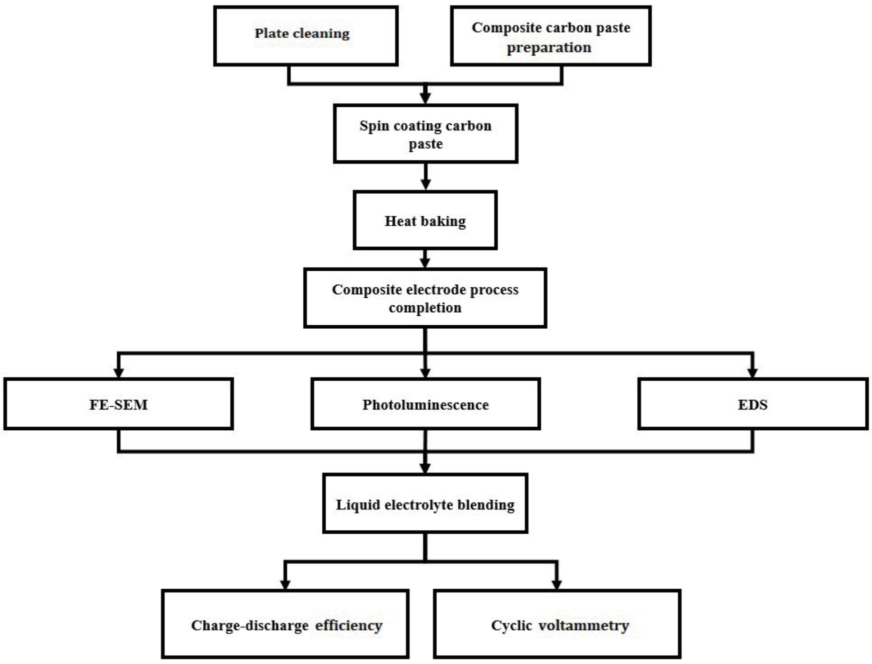


Fig. 1. Flowchart of sample preparation and analysis.

$$C = \frac{dQ}{dV} = \frac{1}{mv\Delta V}\int_{V_1}^{V_2} I(V)\,dV, \tag{1}$$

where $\int_{V1}^{V2} I(V)\,dV$ is the area of hysteresis, v the scanning speed, ΔV the area of voltage, and m the total weight of electrode material.

The CV curve of supercapacitance seemed rectangular. The specific curve was changed by the measurement system in accordance with the type of applied voltage and the rectangular curve. In this study, the supercapacitance of the electrolyte was examined by the charge–discharge test with constant current and the efficiency of the method was calculated using

$$\eta = \frac{Q_{deh}}{Q_{ch}} \times 100\% = \frac{t_{dch}}{t_{ch}} \times 100\%. \tag{2}$$

Here, Q_{deh} is the discharge capacity, Q_{ch} the charge capacity, t_{dch} the time of discharge, and t_{ch} the time of charge.(12,13)

3. Results and Discussion

3.1 Effect of addition of carbon black to supercapacitor

To improve the conductivity of coconut-shell carbon, different amounts of carbon black, namely, 15, 20, 25, 30, and 35 wt%, were added, and the effect on electrode capacitance was determined. Figure 2 shows the surface of the carbon electrode with carbon black. According

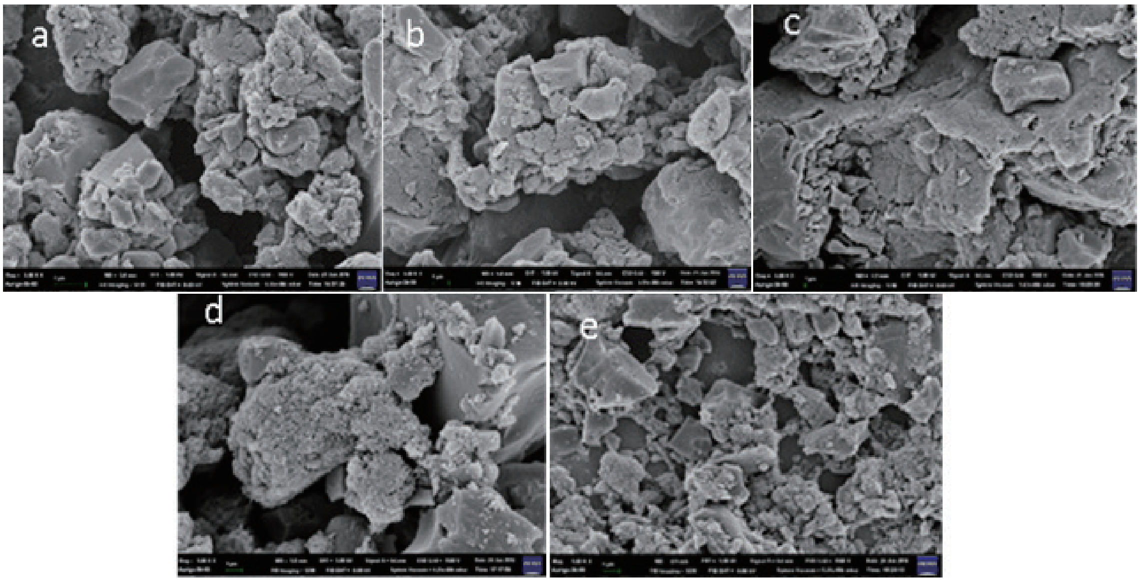


Fig. 2. SEM images of carbon electrode surfaces added with carbon black at (a) 15, (b) 20, (c) 25, (d) 30, and (e) 35 wt%.

to the scanning electron microscopy (SEM) results, tiny 16 nm granules of carbon black are visible on the surface of the carbon electrode when more than 20 wt% was added, and the surface was almost completely covered when 35 wt% carbon black was added. The area of the electrode surface covered by carbon black granules in the former case was much smaller than that in the latter case; therefore, we consider that the addition of more than 30 wt% carbon black caused a decrease in the ratio of the area of visible electrode surface to the electrode surface area covered by carbon black.

Figure 3 shows the CV analysis chart for different amounts of carbon black added. The area of hysteresis increased when the amount of carbon black added increased, but it decreased when the amount of carbon black added reached 30 wt%. The specific capacitance was calculated by referring to the figure and found to reach 54.46 and 73.104 F/g when 15 and 30 wt% carbon black were added, respectively. When the amount of carbon black added reached 35 wt%, excess carbon black was observed and the active carbon surface was covered with excess carbon black reducing both the area of hysteresis and the specific capacitance to 59.23 F/g.

Figure 4 shows the charge–discharge graph for different amounts of carbon black. According to the results of our experiment, the addition of carbon black increases the conductivity. The higher the amount of carbon black added, the higher the charge–discharge efficiency, as shown in Table 1.

3.2 Effect of adding different weights of TiO_2 to supercapacitor

In the experiment of adding different amounts of carbon black, a higher conductivity was achieved at 30 wt%. Therefore, 30 wt% carbon black was added to TiO_2 nanoparticles to obtain

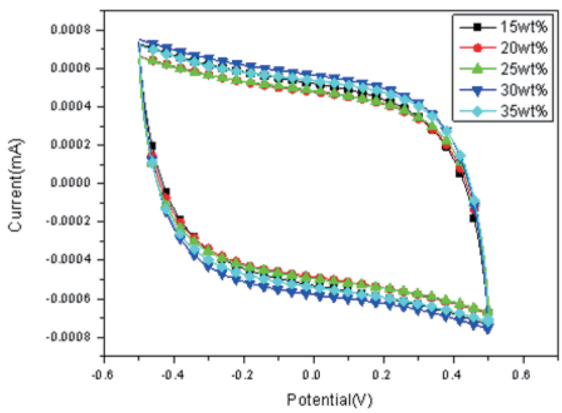


Fig. 3. (Color online) CV analysis chart for different amounts of carbon black added.

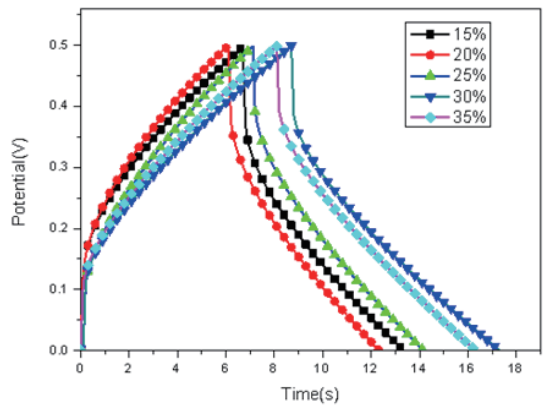


Fig. 4. (Color online) Charge–discharge graph for different amounts of carbon black added.

Table 1
CV and charge–discharge parameters obtained with different amounts of carbon black added.

CB*	$\int_{V1}^{V2} I(V)\,dV$	Capacitance (F/g)	Charge–discharge efficiency (%)
15 wt%	9.8045×10^{-4}	54.46	91.4
20 wt%	9.08×10^{-4}	56.75	95.2
25 wt%	10.6×10^{-4}	64.24	98
30 wt%	9.138×10^{-4}	73.104	98.7
35 wt%	10.07×10^{-4}	59.23	98

*CB: carbon black

different amounts of TiO_2 nanoparticles (15, 20, 25, 30, and 35 wt%). It was found, by SEM surface topography analysis, that TiO_2 increased the surface granule size of electrodes owing to the recombination of TiO_2, as shown in Fig. 5. TiO_2 is considered to be a cheap transition metal with excellent conductivity, stability, and permittivity and bitter electrical properties. The CV charge–discharge analysis was carried out using the parameter of additional TiO_2. The capacitance was higher than those obtained without TiO_2, and the highest capacitance obtained was 96.54 F/g, as shown in Fig. 6 and Table 2. The conductivity decreased when the amount of TiO_2 added was more than 30 wt%, because the porous carbon was covered and the passage of ions was blocked, as shown in Table 2.

3.3 Effect of annealing time on supercapacitor

In this experiment, TiO_2 was added and its disadvantages were determined. To improve the capacitance, annealing was performed at 500 °C for 6, 8, and 10 min to investigate the effect of the annealing time on the supercapacitor. The result shows that the highest capacitance of 171.28 F/g was obtained by adding 30 wt% TiO_2 and annealing at 500 °C for 8 min. According

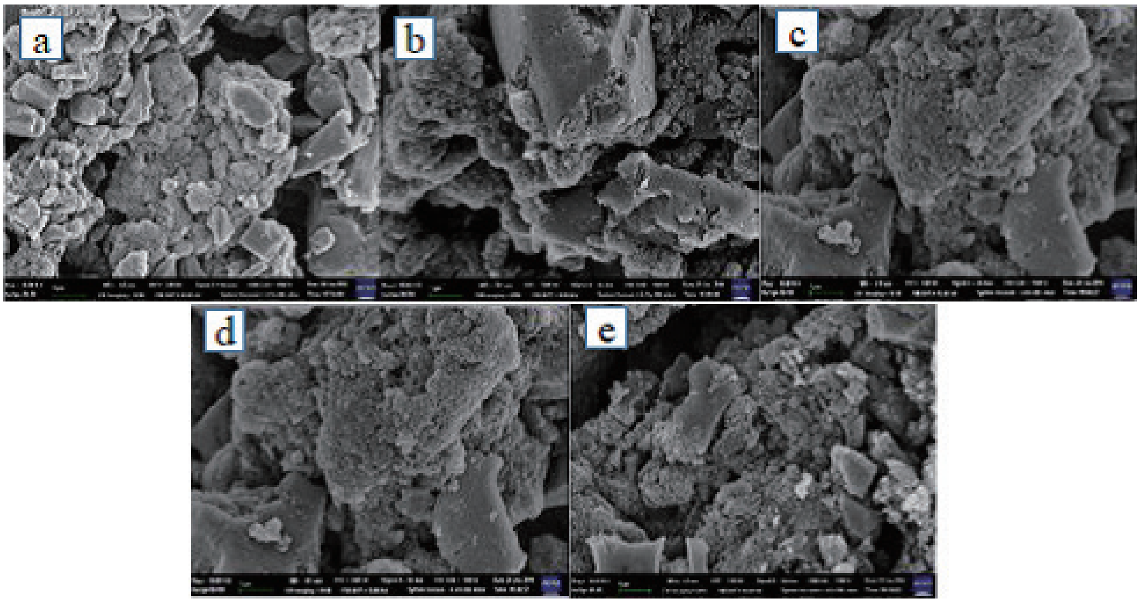
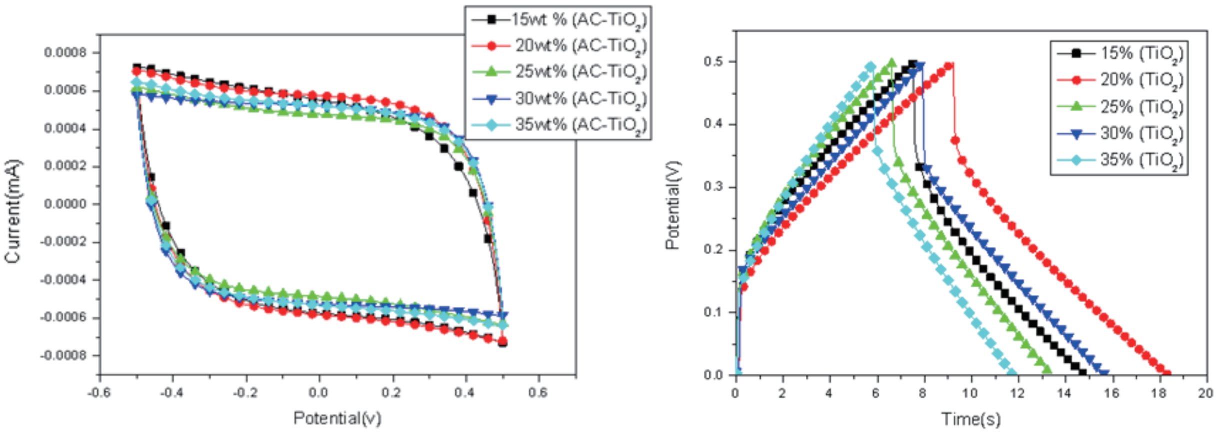


Fig. 5. SEM images of carbon electrode surfaces added with TiO_2 nanoparticles at (a) 15, (b) 20, (c) 25, (d) 30, and (e) 35 wt%.



(a) (b)

Fig. 6. (Color online) Capacitances obtained by adding different amounts of TiO_2. (a) Analysis chart of CV. (b) Analysis chart of constant current.

Table 2
Results of CV charge–discharge analysis with different amounts of TiO_2 added.

CB-TiO_2	$\int_{V1}^{V2} I(V)\,dV$	Capacitance (F/g)	Charge–discharge efficiency (%)
15 wt%	1.033×10^{-3}	66.64	90
20 wt%	1.073×10^{-3}	71.533	97.8
25 wt%	9.168×10^{-4}	83.34	98.4
30 wt%	9.654×10^{-4}	96.54	93.7
35 wt%	7.567×10^{-4}	89.45	89.3

to the SEM results, the crystallinity increased and the gap decreased with annealing. These are the reason why the characteristics of the capacitor improved, as shown in Fig. 7.

With annealing, the amount of oxygen increased markedly in electronic data system (EDS), as shown in Fig. 8. According to the results of CV and constant current analyses, the capacitance improved after the addition of TiO_2 and rapid thermal annealing (RTA). The highest capacitance was obtained with annealing at 500 °C for 8 min, as shown in Fig. 9 and Table 3.

Figure 10 shows photoluminescence (PL) in the case of adding 30 wt% TiO_2 and annealing at 500 °C for 6, 8, and 10 min. The amount of oxygen decreased markedly with the addition of TiO_2 and annealing. This result shows that the highest capacitance of 171.28 F/g was obtained by adding 30 wt% TiO_2 and annealing at 500 °C for 8 min.

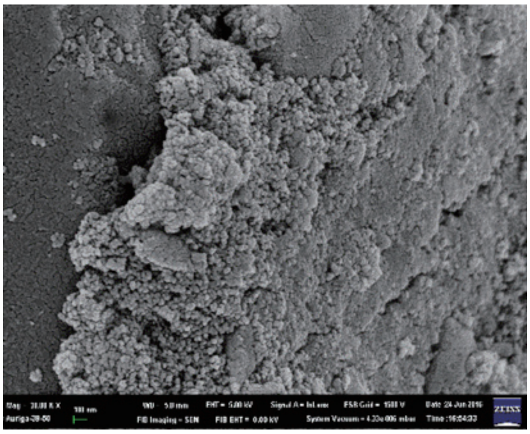


Fig. 7. SEM images of carbon electrode surface added with 30 wt% TiO_2 followed by annealing at 500 °C.

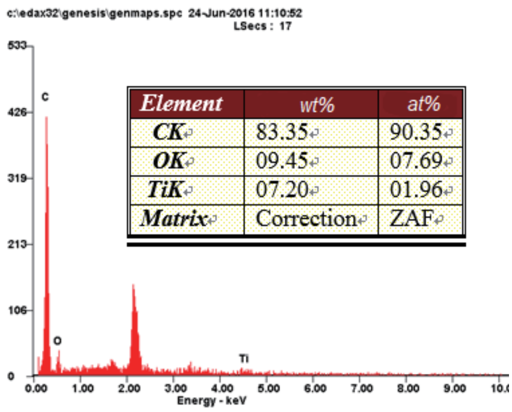
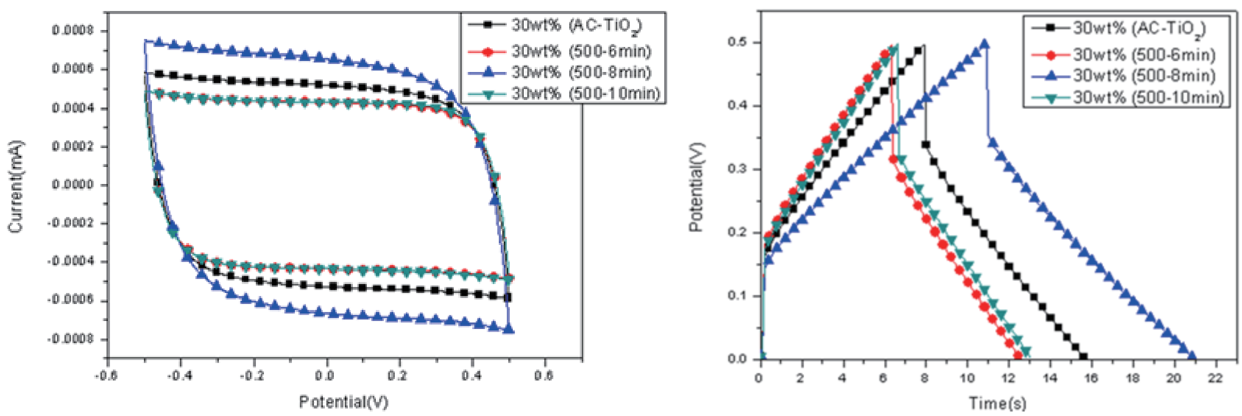


Fig. 8. (Color online) EDS X-ray spectrum of carbon electrode with addition of 30 wt% TiO_2 and annealing at 500 °C for 8 min.



(a) (b)

Fig. 9. (Color online) Capacitances obtained by adding 30 wt% TiO_2 and annealing at 500 °C for 6, 8, and 10 min. (a) Analysis chart of CV. (b) Analysis chart of constant current.

Table 3
Results of CV and charge-discharge analyses after adding TiO_2 and annealing at 500 °C for different times.

		Not annealed	500 °C 6 min	500 °C 8 min	500 °C 10 min
AC-TiO_2 30 wt%	$\int_{V1}^{V2} I(V)\,dV$	9.65×10^{-4}	8.127×10^{-4}	11.99×10^{-4}	8.16×10^{-4}
	Capacitance (F/g)	96.54	135.45	171.28	136.11
	Charge–discharge efficiency (%)	96.2%	92.3%	90.9%	100%

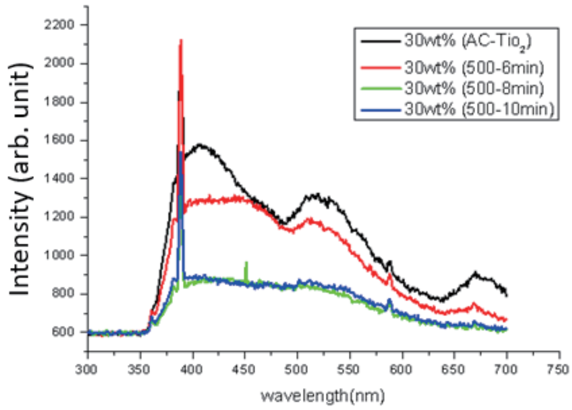


Fig. 10. (Color online) Fluorescent graph of photoexcitation after adding 30 wt% TiO_2 and annealing at 500 °C for 6, 8, and 10 min.

4. Conclusions

This study was conducted to produce a TiO_2 supercapacitor. This supercapacitor was evaluated by field emission SEM, EDS, CV, charge–discharge, and PL measurements. First, the effect of the addition of conductive carbon black to electrodes was determined. The CV measurement showed that the highest capacitance of 73.104 F/g was obtained when 30 wt% conductive carbon black was added. Second, considering 30 wt% conductive carbon black as the optimal amount, the effect of further adding different amounts of TiO_2 on the capacitance was investigated. According to experimental results, the highest capacitance of 96.54 F/g was obtained when 30 wt% TiO_2 was added. Third, the addition of 30 wt% TiO_2 and rapid thermal annealing at 500 °C for 6, 8, and 10 min were observed to eliminate oxygen deficiency and increase the capacitance. These results showed that the highest capacitance of 171.28 F/g and the lowest oxygen deficiency were obtained by annealing at 500 °C for 8 min.

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