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# Reduced graphene oxide/Titanium oxide nanocomposite synthesis via microwave-assisted method and supercapacitor behaviors

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ABSTRACT

In this paper, graphene oxide (GO) was firstly synthesized by modification of Hummers method from the literature. Secondly, reduced graphene oxide (rGO)/Titanium oxide ($TiO_2$) nanocomposites were synthesized with different wt/wt % of GO/$TiO_2$ (1:1; 1:2; 1:5 and 1:10) by microwave-assisted method. By treating GO and GO/$TiO_2$ nanocomposites in a microwave oven, reduced graphene oxide (rGO) and rGO/$TiO_2$ materials could be obtained within power of 180 W in 10 min. The weight ratio of rGO and $TiO_2$ was used to obtain the optimum conditions for nanocomposite materials. The rGO/$TiO_2$ nanocomposite active materials were characterized by cyclic voltammetry (CV), Fourier-transform infrared – Attenuated total reflectance (FTIR-ATR), scanning electron microscopy-energy dispersion X-ray (SEM-EDX), thermogravimetry (TGA), differential thermal analyzer (DTA) and electrochemical impedance spectroscopy (EIS) analysis. Thirdly, supercapacitors were fabricated as a symmetric device with two electrode configuration. The device performances were tested by CV, galvanostatic constant current (CC), and EIS measurements. TGA analysis indicated that the thermal stability of the nanocomposites improved from rGO (40% at 892.8 °C) to nanocomposite as the initial feed ratio of $[GO]_o/[TiO_2]_o = 1/10$ as (94% at 949.3 °C) increased.

The result show that the as-prepared symmetrical rGO/$TiO_2$ nanocomposite on the two-electrode system displays very high specific capacitance of 524.02 F/g at 2 mV/s for $[GO]_o/[TiO_2]_o = 1/5$ with a high energy density of E = 50.07 Wh/kg at 2 mV/s for $[GO]_o/[TiO_2]_o = 1/1$ and high power density of P = 58.6 kW/kg at a the scan rate 1000 mV/s for $[GO]_o/[TiO_2]_o = 1/1$. Additionally, the symmetric electrode shows good cycling stability with a retention value of 6.6% for $[GO]_o/[TiO_2]_o = 1/1$ after 1000 cycles. These good results suggest us that rGO/$TiO_2$ nanocomposite which is obtained by microwave-assisted method has a great potential as an electrode material for supercapacitor applications.

The equivalent circuit model of $R_s(C_{dl}(R_{ct}W))$ was used to explain parameters of solution resistance, double layer capacitance ($C_{dl}$), charge transfer resistance ($R_{ct}$), Warburg impedance (W). Theoretical and experimental values support with each other.



## 1. Introduction

Graphite is a well-known natural mineral [1]. Graphene is another member of the graphene oxide (GO) which is a derivative of graphite. GO can be reduced by different reduction methods. Xiong et al. [2] have synthesized supercapacitor with reduced graphene oxide (rGO)-$TiO_2$ nanocomposite via hydrothermal method. A specific capacitance of rGO/$TiO_2$ nanocomposite was obtained by the variation value between ~60 and 200 F/g, at a scan rate of 2 mV/s. Graphene is used as an active electrode material for supercapacitors with a theoretical specific surface area (~2630 $m^2$/g) with low resistance ($10^{-6}$ 'Ω.cm) and high mechanical resistance and chemical stability [3,4]. Graphene has many advantageous such as high thermal conductivity, electrical conductivity, strength [5], and high specific area [6].

$TiO_2$ is an important metal oxide for supercapacitors because of its easy synthesis, high energy density capability, low cost, non-toxicity, environmental friendliness and high purity [7]. $TiO_2$ is n-type semiconductor and used in many applications, such as solar cells [8], hydrogen production [9] and energy storage devices [10],

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supercapacitors [11–13] and batteries [14,15]. Tang et al. [16] have studied amorphous crystalline $TiO_2$/carbon nanofibers (CNFs) composite electrode by one-step electrospinning method. Hybrid Ti@CNFs, where $TiO_2$ had amorphous, tetragonal rutile and anatase structure. It has low charge transfer resistance ($R_{ct}$ = 0.34 Ω) and high specific capacitance ($C_{sp}$ = 280.3 F/g, at current density of 1 A/g).

rGO-based nanocomposites have been used for supercapacitor electrochemical performances [17,18]. In literature, many carbon based materials, such as activated carbon electrodes from biomass [19,20], carbon nanotubes [21], graphene [22] and graphite-like carbon nitrite [23], etc.

Microwave irradiation can heat the nanocomposite with high temperature in a short amount of time by transferring energy to solvent [24]. As a result, this technique has advantageous, such as mass production in a short time and low energy cost [25–27]. Microwave irradiation is an efficient, eco-friendly and non-contacting heating method [28]. It can be used in organic synthesis [29], material formation [30], polymer chemistry [31] and the synthesis of nanoparticles [32]. Microwave irradiation technique was named as microwave-hydrothermal method [33]. In literature, there are many chemical reductions using agents, such as hydrazine [34,35] or dimethylhydrazine [36,37], hydroquinone [38], and $NaHB_4$ [39] have been used to reduce GO or graphene oxide exfoliated from GO.

Supercapacitors, also named electrochemical capacitors or ultracapacitors, have attracted more attention over the last years because of their higher energy and power density and longer cycle life than secondary batteries [40–42]. Generally, supercapacitors are divided into two catagories: double layer capacitor electrode and pseudocapacitive electrode materials [43]. In our paper, we used double layer capacitor electrode which is used reduced graphene oxide.

In this study, rGO/$TiO_2$ composites were successfully synthesized via microwave-assisted reduction of GO in $TiO_2$ suspensions using a microwave system. These nanocomposites in different feed ratios of rGO/$TiO_2$ (1/1; 1/2; 1/5; 1/10) were used in electrode materials for supercapacitor performances of nanocomposite materials.

The aim of this study is to obtain rectangular box shape via cyclic voltammetry (CV), fast reflect of oxidation/reduction on high current changes, low-charge transfer resistance, long cycle life for the designed supercapacitor fabrication. Moreover, galvanostatic charge/discharge, constant current and electrochemical impedance spectroscopic measurements were taken for rGO and rGO/$TiO_2$ nanocomposites.

## 2. Experimental

### 2.1. Materials

Titanium oxide ($TiO_2$, >99.99) was obtained from Merck, graphite, sulfuric acid ($H_2SO_4$, >98.0), hydrochloric acid (HCl, >98.0), sodium hydroxide (NaOH, >98.0), hydrogen peroxide ($H_2O_2$, >98.0), ammonia ($NH_3$, >98.0) acetone ($C_3H_6O$), potassium permanganate ($KMnO_4$), methyl alcohol ($CH_3OH$, >99.5%), ethyl alcohol ($C_2H_5OH$, >96.0%), stainless steel for electrode construction, membrane (Celgard 3501), Kapton type band, Microscope slides and materials were obtained from Sigma-Aldrich.

### 2.2. Instrumentation

Cyclic voltammetry (CV), galvanostatic charge/discharge (CC) and electrochemical impedance spectroscopy (EIS) measurements were tested by Ivium-vertex potentiostat/galvanostat instrument at room temperature. The electrical experiments were carried out using a two-electrode system. The samples were directly served as a stainless steel working electrode and a counter electrode. CV measurements were performed the scan rates from 2 mV/s to 1000 mV/s. CC measurements were taken by at current densities of 0.1, 0.2, 0.5, 1, 2, 5 and 10 mA at the weight of 23, 9.8, 10.1, 7.4 and 32 mg. Furthermore, EIS measurements were carried out a frequency range from 100 kHz to 10 mHz with ac perturbation of 10 mV.

Fourier transform infrared spectroscopy-attenuated total reflectance spectroscopy (FTIR-ATR, Perkin Elmer), and the scanning electron microscopy (SEM-EDX, EVO LS 10) were measured by spectroscopic and morphologic analysis.

Thermogravimetry and Differential Thermal Analyzer (TG-DTA, EXSTAR 6300) was used to measure of TGA and DTA plots. Pellet machine (Graseby Specac) was used to obtain as an active electrode material for supercapacitor device fabrication.

### 2.3. Microwave irradiation experiments

The microwave oven used in this article is a commercially available Samsung microwave oven. The microwave output of this oven is at 1150 W and 2450 MHz. A full homogeneous solution is used for every microwave irradiation experiments. All the microwave irradiation experiments were performed in a microwave oven. In a typical experiment, a 100% irradiation power at 180 W and a 10 min treatment period were used [44].

### 2.4. Fabrication of rGO/$TiO_2$ composite for supercapacitor device

Supercapacitor devices were designed symmetrically to measure CV, CC and EIS tests. To obtain the supercapacitor device, we used two stainless steel (SS) electrodes as a current collector and rGO/$TiO_2$ films which were reduced by microwave-assisted method on various feed ratios of [GO]/[$TiO_2$] as [GO]/[$TiO_2$] = 1/1,1/2, 1/5, 1/10. Electrodes do not include additional binders or conductive additives [45]. A separator (Celgard 3501, Celgard, Charlotte, NC) was sandwiched between two identical pieces of rGO/$TiO_2$ films in a layered structure. This layered assembly was wrapped with Kapton tape and then dipped in the electrolyte. Electrochemical measurements were taken by Iviumstat potentiostat/Galvanostat using alligator clips.

### 2.5. Synthesis of graphene oxide (GO)

Graphene oxide (GO) was synthesized from graphite using the modified Hummers method, which is different from literature [46] using concentrated sulfuric acid, temperature and waiting time for reactions. In the synthesis procedure, 3 g graphite and 70 mL concentrated $H_2SO_4$ were dispersed in the same vessel using ice bath and stirred for ~4 h. And then ~9 g potassium permanganate ($KMnO_4$) was slowly added and stirred constantly. To avoid potential explosion, suspension's temperature was kept under the 20 °C and suspension stirred for 3 h. Then, suspension's temperature was increased from 20 °C to 35 °C and added 150 mL de-ionized water. In the last step of increasing temperature, its temperature was increased to 97 °C in 30 min. By using magnetic stirrer for suspension for a night, it was cooled to room temperature. 500 ml de-ionized water was added and suspension temperature was adjusted under 15 °C using ice bath. 10 mL 30% $H_2O_2$ was slowly added and constant speed stirring for 4 h to complete the reaction. Suspension was evaluated the centrifuge at 4000 rpm for 15 min. When the precipitate was formed, the liquid was slowly poured out from the side of the flask and precipitate washed with de-ionized water. Precipitate was repeatedly centrifuged and