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Novel RGO-$ZnWO_4$-Fe_3O_4 Electrodes Material for Energy Storage Device Applications

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Abstract: As the global concerns in the development of human civilization, the scientific and technological issues of energy utilization and environment protection are currently facing challenges. Nowadays, enormous energy demands of the world are mainly met by the non-renewable and environmental unfriendly fossil fuels. To replace the conventional energy platform, a pursuit of renewable and clean energy sources and carriers, including hydrogen storage, lithium batteries, and supercapacitors. Electrochemical capacitors, also called supercapacitors, store energy using either ion adsorption (electrochemical double layer capacitors) or fast surface redox reactions (pseudo-capacitors). They can complement or replace batteries in electrical energy storage and harvesting applications, when high power delivery or uptake is needed. A notable improvement in performance has been achieved through recent advances in understanding charge storage mechanisms and the development of advanced nanostructured materials. Herein, we report novel RGO-$ZnWO_4$-Fe_3O_4 electrodes material can be synthesized using one step microwave irradiation technique and reported as an electrode material for supercapacitors applications. The surface morphology, chemical composition and electronic structure of the RGO-$ZnWO_4$-Fe_3O_4 electrodes were characterized using X-ray diffraction (XRD), transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS) techniques. The electrochemical performance of the RGO-$ZnWO_4$-Fe_3O_4 electrodes has been investigated using cyclic voltammetry (CV) techniques. The result reveals that a specific capacitance of 480 F/g, an energy density of 15 Wh/kg and power density of 1719.5 W/kg is observed over RGO-$ZnWO_4$-Fe_3O_4 electrodes materials. The cost effective electrodes materials of RGO-$ZnWO_4$-Fe_3O_4 can be useful for future electrochemical energy storage device applications.

Keywords: Microwave Irradiation Method, Electrochemical Properties, RGO-$ZnWO_4$-Fe_3O_4 Electrodes, Supercapacitors

1. Introduction

In recent years, researchers are developing advanced nanostructured materials for energy conversion and storage devices for example battery and supercapacitors. The growth of alternative energy storage devices in mix with the present battery and supercapacitor will apparently satisfy the effective responses for energy storage. Among various flexible energy storage devices, supercapacitors with engaging properties, for instance, eco-friendly operation, quick charge-discharge limit, high power density and long lifetime, are considered as the most promising future energy storage devices to fulfill the rapidly growing power demand [1, 2]. Supercapacitors are expanding mind blowing specific and mechanical thought due to their promising applications in auto and flexible electronic frameworks including electric vehicles, memory devices, microelectromechanical systems, digital cameras, mobile phones, and pacemakers [3, 4]. Till now, extraordinary sorts of materials are used as electrode materials which include conducting polymers, carbonaceous materials, and transition metal oxides [5, 6]. In any case, low abundance and high cost hindered their current era. To solve these problems, we have to develop a high-performance energy storage material by using a simple and cost efficient method.

To the best of our knowledge, Reduced graphene oxide-Zinc tungstate-Iron oxide composite as a supercapacitor electrode materials not yet reported. In this research work,

RGO-$ZnWO_4$-Fe_3O_4 can be synthesized by facile microwave irradiation method. The characterize phase, purity, morphology and chemical composition of the RGO-$ZnWO_4$-Fe_3O_4 were established by X-ray diffraction (XRD), transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS) techniques. Furthermore, an electrochemical property of the RGO-$ZnWO_4$-Fe_3O_4 was carried out and the result reveals that the as-prepared RGO-$ZnWO_4$-Fe_3O_4 is the promising candidate which can act as an electrode material for supercapacitor applications.

2. Experimental

2.1. Materials

The entire chemicals were purchased from analytical grade and used as received without further purification. All the experimental solutions were prepared with deionized (DI) water.

2.2. Synthesis of RGO-$ZnWO_4$-Fe_3O_4 Nanocomposites

Graphene oxide (GO) was synthesized from graphite flasks via modified Hummers method [7]. RGO-$ZnWO_4$-Fe_3O_4 nanocomposite was produced by a one-step microwave irradiation approach as reported previously [8, 9]. In briefly, a certain amount of GO was dispersed into 48.5 ml of ethylene glycol solution with ultrasonic treatment for about 30 minutes and 50 ml of zinc acetate solution (0.05 M) and 50 ml of sodium tungstate solution (0.05 M) was slowly added to the GO suspension and maintained the pH-9.0 of the solution using ammonia. After the mixture was irradiated at the microwave for 10 minutes at 350 W and the obtained RGO-$ZnWO_4$ mixture was cooled to room temperature. Then, 0.01 M of iron acetate (50 ml of ethanol and DI water mixture) and ammonia (10 ml) was slowly introduced into the above mixture under stirring for about 30 minutes and once again treated with microwave irradiation at 350 W for 10 minutes. The obtained blackish precipitate of RGO-$ZnWO_4$-Fe_3O_4 nanocomposites was collected and washed with dilute ethanol several times. Finally, the obtained RGO-$ZnWO_4$-Fe_3O_4 was dried in vacuum oven at 80 ^oC for about 12 hours. For the control experiment, a similar procedure was carried out with required precursor and denoted as RGO, $ZnWO_4$, and RGO-$ZnWO_4$.

2.3. Characterization

The crystalline nature, surface morphology and chemical compositions of the as-synthesized nanocomposites was examined by the X-ray diffraction (XRD, Rigaku, Japan), transmission electron microscope (TEM, JEM 200CX, JEOL, Japan) and X-ray photoelectron spectroscopy (XPS, MultiLab2000, Thermo VG Scientific System, UK).

2.4. Electrochemical Measurements

The working electrode can be prepared by mixing an electro-active material, acetylene black and 5% Nafion, with a ratio of 75:15:10. This mixture was dispersed in 1ml of isopropanol by ultrasonication for 10 minutes. The electrodes were prepared by coating dispersed materials on a 1 cm x 1 cm sized stainless steel using a layer-by-layer brush coating technique and dried in a vacuum oven at 80°C for 6 hours. The weight of electrode material was 2 mg. The supercapacitor setup consists of RGO-$ZnWO_4$-Fe_3O_4 coated stainless steel electrodes as current collectors, a filter paper as a separator and 0.5 M Na_2SO_4 solution act as an electrolyte. The separator rinsed with 0.5 M Na_2SO_4 was sandwiched between two stainless steel electrodes as current collectors. The electrochemical measurements were performed by cyclic voltammetry (CV) using an Ivium Stat electrochemical workstation (IVIUM Technologies, Netherlands). The CV measurements was carried out between 0 - 0.5 V at different scan rates of 10 - 200 mV/s.

3. Results and Discussion

3.1. Structural, Morphology and Elemental Composition Analysis

The powder X-ray diffraction pattern reveals the formation of the RGO-$ZnWO_4$-Fe_3O_4 nanocomposite, as shown in Figure 1. The XRD pattern shows $ZnWO_4$ (JCPDS File No. 15-0774) and Fe_3O_4 (JCPDS File No. 19-0629) and there is no obvious diffraction peak of RGO at about 23° is not detected within the XRD patterns of RGO-$ZnWO_4$-Fe_3O_4 composite, indicating that significant formation of RGO-$ZnWO_4$-Fe_3O_4 composite face-to-face stacking is absent due to the introduction of $ZnWO_4$ and Fe_3O_4 on both sides of RGO sheets.

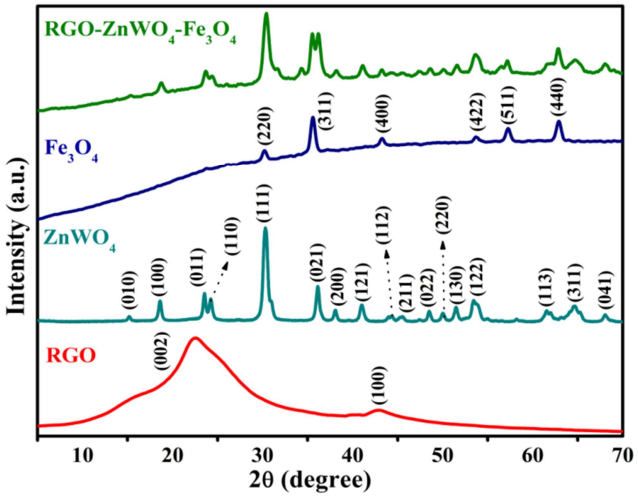

Figure 1. *XRD spectrum of as-synthesized RGO-$ZnWO_4$-Fe_3O_4.*

TEM image of RGO-$ZnWO_4$-Fe_3O_4 (Figure 2) clearly demonstrated that the layered $ZnWO_4$ and Fe_3O_4 are anchored on the surface of the crumpled RGO nanosheets successfully. Due to their extremely small size and aggregated of the nanomaterials, the $ZnWO_4$ and Fe_3O_4 were observed as pointed by the arrows.

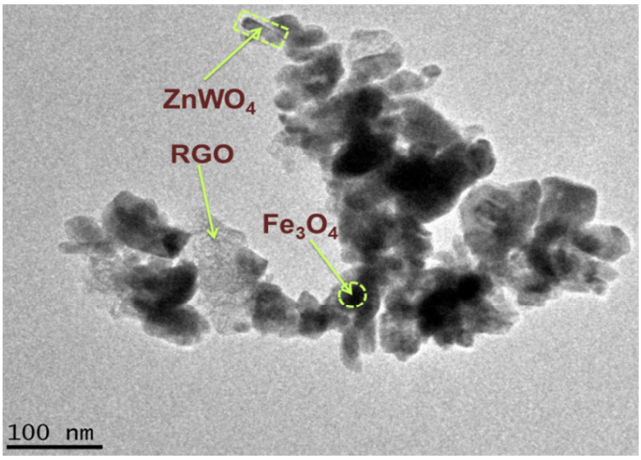

Figure 2. *TEM image of as-synthesized RGO-$ZnWO_4$-Fe_3O_4.*

The XPS spectrum of the as-prepared RGO-$ZnWO_4$-Fe_3O_4 nanocomposite is shown in Figure 3. Figure 3a shows the general survey spectra of the as-prepared RGO-$ZnWO_4$-Fe_3O_4 nanocomposite which displays that the surfaces contain C, Zn, W, Fe, and O. Figure 3b illustrates the C 1s spectral region, which could be deconvoluted into four peaks with binding energies of 284.8 eV, 286.6 eV, 288.1 eV and 290.1 eV. These peaks are assigned to sp2 C-C/C=C bonds in the aromatic ring, C-O, C=O and O-C=O bonds in the oxygenated functional groups respectively which indicates that GO has been reduced to graphene sheets [4]. Figure 3c displays the Zn 2p region, composed of two peaks at 1019.1 eV and 1041.9eV which corresponds to the Zn $2p_{3/2}$ and Zn $2p_{1/2}$ state, respectively [10]. Figure 3d depicts the W 4f region, consisting of two peaks at 36.8 eV and 38.8 eV are assigned to W $4f_{7/2}$ and W $4f_{5/2}$ [11]. These results are consistent with the previously reported values for $ZnWO_4$ [12]. Figure 3e portrays binding energies of Fe 2p region, two peaks are found at 709.2 eV and 723.5 eV corresponding to Fe $2p_{3/2}$ and Fe $2p_{1/2}$, indicating that Fe_3O_4 particles [13]. Figure 3f shows the O 1s spectra region, which could be deconvoluted into two peaks of binding energies of values, 529.9 eV and 531.6 eV corresponding to Fe-O and W-O-W, respectively [14]. The above results show that $ZnWO_4$ and Fe_3O_4 particles are well decorated on RGO sheets successfully.

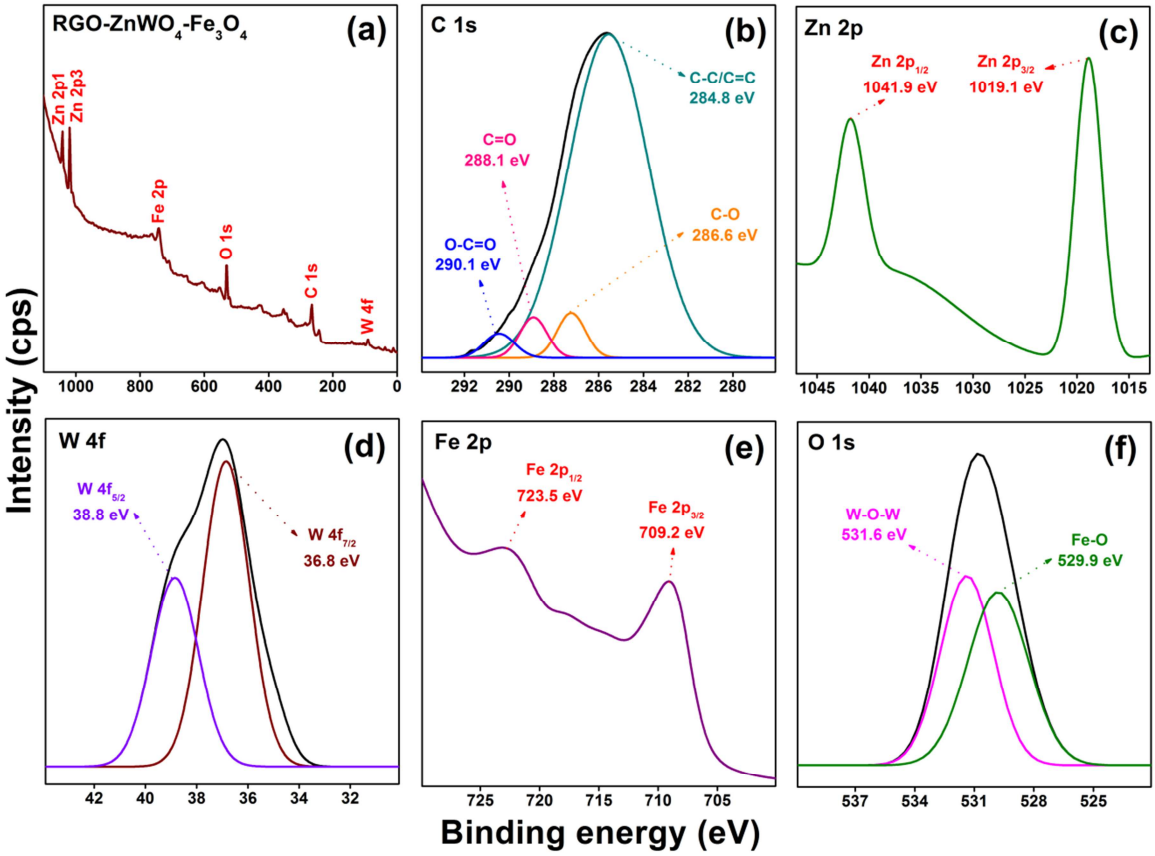

Figure 3. *XPS spectrum of as-synthesized RGO-$ZnWO_4$-Fe_3O_4.*

3.2. Electrochemical Analysis

The electrochemical behaviors of the active electrode materials were investigated in two electrode symmetry of 0.5 M Na_2SO_4 by cyclic voltammetry (CV) measurements. Figure 4a displays the CV curves of RGO, $ZnWO_4$, RGO-$ZnWO_4$ and RGO-$ZnWO_4$-Fe_3O_4 electrodes were measured at a scan rate of 50 mV/s with operating voltage of 0 - 0.5 V. From these CV plots, all the four curves show at rectangular in shape, which is indicating its EDLC behavior of all the samples. The specific capacitance (*Cs*) [15] of the all electrode materials are measured from CV curves by the equation (1).

$$Cs = 2 * \left(\frac{I}{m*V*\left(\frac{dv}{dt}\right)}\right) \quad (1)$$

Where I is the average current during the anodic and cathodic sweep current, V is the potential window, $\frac{dv}{dt}$ is the scan rate and m is the mass of the electrode material.

The calculated specific capacitances of RGO, $ZnWO_4$, RGO-$ZnWO_4$ and RGO-$ZnWO_4$-Fe_3O_4 electrodes are 125.9, 42.2, 191.4 and 202.2 F/g at the scan rate of 50 mV/s, respectively. The enhancement of the electrochemical performance of RGO-$ZnWO_4$-Fe_3O_4 may be ascribed to the synergy effect between $ZnWO_4$ and Fe_3O_4 on the RGO sheets. The good dispersion of $ZnWO_4$ and Fe_3O_4 on the surface of the RGO can avoid the aggregation of both which are leading to the higher active surface area for charge storage [16]. Therefore, among the RGO-$ZnWO_4$-Fe_3O_4 fulfilled the highest capacitance instead of RGO, $ZnWO_4$ and RGO-$ZnWO_4$.

The CV curves under different scanning rates at 10 - 200 mV/s for RGO-$ZnWO_4$-Fe_3O_4 are shown in Figure 4b. The increasing of the scanning rates and the slight deviation in the CV curves shapes of RGO-$ZnWO_4$-Fe_3O_4, which is due to the low interaction between the electrolyte ions and electrode. The calculated specific capacitances of the RGO-$ZnWO_4$-Fe_3O_4 are 480, 313.3, 202.2, 177.9 and 137.6 F/g at different scan rates of 10, 30, 50, 100 and 200 mV/s are shown in Figure 4c, respectively.

The two most important factors of the energy storage devices are the energy density and power density. Ragone plots are used to demonstrate the energy density as a function of power density. The energy density (E) [17] and power density (P) [18] of RGO-$ZnWO_4$-Fe_3O_4 electrodes are measured by following equations (2) and (3).

$$E = \left(\frac{1}{8}\right) * Cs * V^2 \quad (2)$$

$$P = \left(\frac{E}{V}\right) * \left(\frac{dv}{dt}\right) \quad (3)$$

Where Cs is the specific capacitance measured by CV and V is the potential window and $\frac{dv}{dt}$ is the scan rate.

The calculated energy density of the RGO-$ZnWO_4$-Fe_3O_4 is 15, 9.8, 6.3, 5.6 and 4.3 Wh/kg and power density value is 300, 587.4, 725, 1112.3 and 1719.5 W/kg at different scan rates of 10, 30, 50, 100 and 200 mV/s are shown in Figure 4d, respectively.

Figure 4d shows the Ragone plot of RGO-$ZnWO_4$-Fe_3O_4 electrodes show maximum performance with the highest energy density of 15 Wh/kg at a scan rate of 10 mV/s and power density of 1719.5 W/kg at a scan rate of 200 mV/s. The above results confirming that the RGO-$ZnWO_4$-Fe_3O_4 may be a suitable electrode material for high-performance supercapacitor applications.

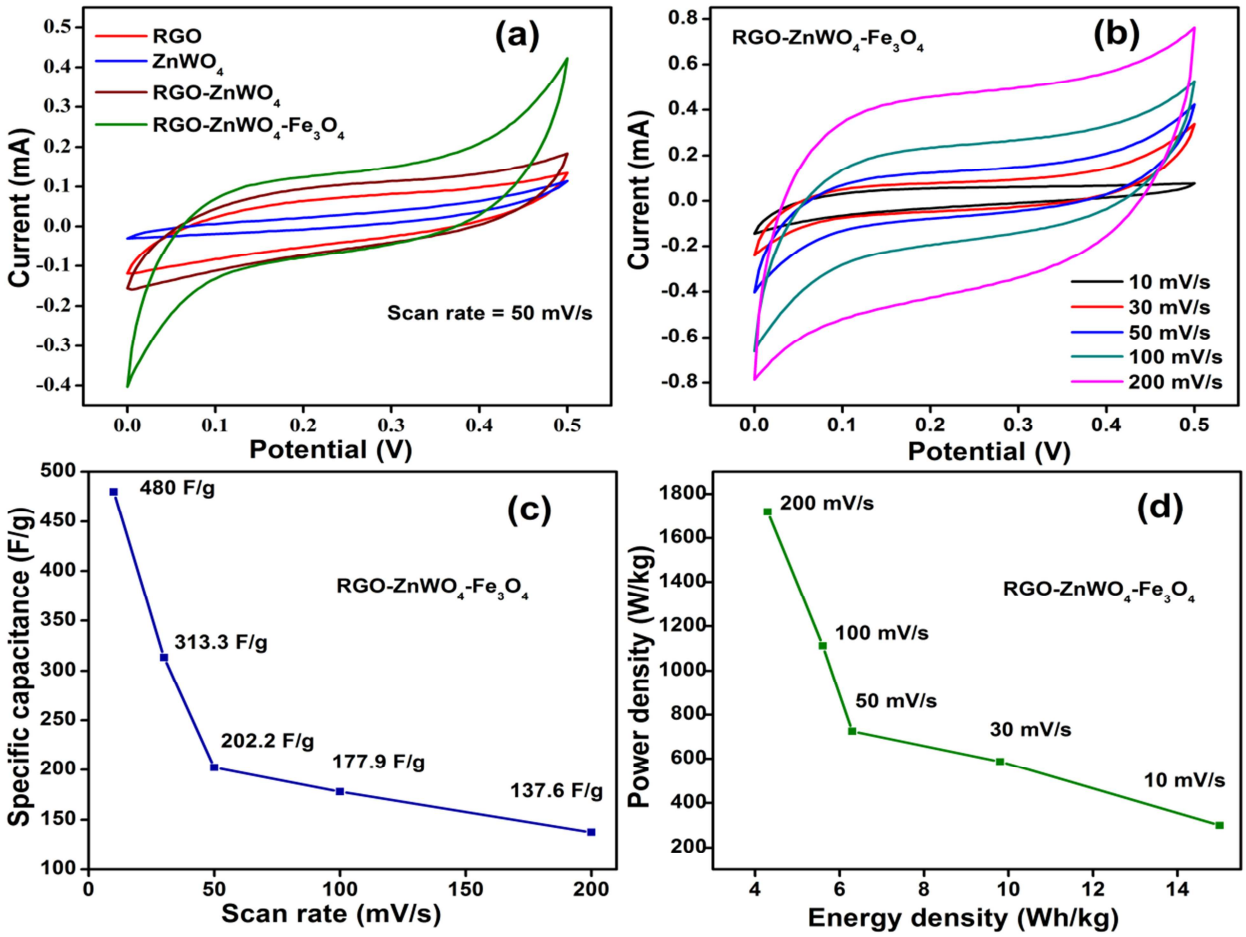

Figure 4. *(a, b) Cyclic voltammograms, (c) Specific capacitance and (d) Ragone plot of RGO-$ZnWO_4$-Fe_3O_4.*

4. Conclusions

In summary, we report a microwave irradiation method for the synthesis of RGO-$ZnWO_4$-Fe_3O_4 electrode material for supercapacitor applications. The crystal structure, morphology and elemental composition of as-synthesized nanocomposite were investigated by XRD, XPS, and HRTEM. The as-synthesized RGO-$ZnWO_4$-Fe_3O_4 electrode material showed excellent electrochemical performance in terms of high specific capacitance (480 F/g), an energy density (15 Wh/kg) and power density (1719.5 W/kg). Therefore, the RGO-$ZnWO_4$-Fe_3O_4 may be a capable electrode material for high-performance supercapacitors. Hence, this novel approach is a low-cost route for the large-scale synthesis of high-quality RGO-$ZnWO_4$-Fe_3O_4 electrode materials for future energy storage device applications.

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