

Original Research Paper

Hydrothermal Synthesis of CuWO_4 -Reduced Graphene Oxide Hybrids and Supercapacitor Application

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Article history

Received: 15-07-2016

Revised: 08-08-2016

Accepted: 09-08-2016

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Abstract: This study reports a facile hydrothermal synthesis of Copper tungsten oxide (CuWO_4) and CuWO_4 -reduced graphene oxide hybrid nanoparticles and its application as an electrode for supercapacitor application. The morphology and composition has been characterized using X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and EDAX. The supercapacitive behavior has been studied from cyclic voltammetry and galvanostatic charge-discharge tests. The CuWO_4 -reduced graphene oxide hybrid nanoparticles show highest specific capacitance of 35.71 F/g at a current density of 0.25 A/g with excellent cycling stability.

Keywords: Nanoparticle, CuWO_4 -Reduced Graphene Oxide, Supercapacitor

Introduction

The rising consumption of energy and the rapid depletion of global energy resources have made researchers (Dresselhaus and Thomas, 2001; Eisenberg and Nocera, 2005) to develop alternate energy sources. The need for clean and sustainable energy sources has always attracted the scientific community to develop (Liu *et al.*, 2010a; Pushparaj *et al.*, 2007; Rakhi *et al.*, 2012) highly efficient energy storing devices. In the past decade the rapid growth in human population, advancement of hybrid electronic devices and exhaustion of energy sources have given many highly performing (Yang *et al.*, 2011; Aricol *et al.*, 2005) energy storage devices. Among various energy storage systems, supercapacitor also known as ultracapacitor or electrochemical capacitor has acquired the electronics market due to its fast charge-discharge rate, long cycle life, high power density and high reliability. Compared to battery and fuel cells the supercapacitor (Gao, 2005) has successfully fulfilled the need for (Khaligh and Li, 2010) energy backup systems, consumer portable devices and electrical hybrid automobiles. To design high performing supercapacitor (Yan *et al.*, 2014) many criteria are taken into consideration such as high specific capacitance, large rate capability, high cycle stability, toxicity and the cost of the material.

Supercapacitors are categorized into two classes (Halper and Ellenbogen, 2006; Cultura II and Salameh, 2015) based on their energy storing mechanisms (i) Electrochemical Double Layer Capacitors (EDLCs) (ii)

pseudocapacitors. EDLC (Yoon *et al.*, 2004) stores charge physically through electrostatic mechanism or non faradic process, while pseudocapacitor (Conway *et al.*, 1997) stores charge chemically through redox reactions known as faradic process. For high performing EDLC (Kim *et al.*, 2006) specific surface area, electrical conductivity, pore size and distribution are taken into consideration. For EDLCs, capacitance values are directly proportional to electrode surface area. Hence, increase of surface area (Lota *et al.*, 2008) is of primary importance for obtaining increased content of the energy stored. For pseudocapacitors (Lu and Zhou, 2011; Nithya *et al.*, 2013; Wu *et al.*, 2011) increase of active material usage in a redox reaction is of primary importance for increasing pseudo-capacitance values. So, activated carbon, CNTs, mesoporous carbon or generally porous carbon materials are used as EDLC while transition metal oxides, conducting polymers are used as pseudocapacitors.

Metaloxides (Wang *et al.*, 2015; Yuan *et al.*, 2014) are highly used to develop high performing supercapacitor. RuO_2 shows specific capacitance of 1585 F/g (Ponrouch *et al.*, 2013) but due to its toxicity and high cost synthesis, the investigation for novel, low cost, environment friendly material is still going on. Nanostructuring (Chen *et al.*, 2013; Wua *et al.*, 2015; Yu *et al.*, 2015) the materials is a reasonable method to improve the supercapacitance of the material. Among many nanomaterials CuWO_4 (Kumar and Karuppuchamy, 2014; Kumar *et al.*, 2015) is a promising material for supercapacitor. It is also used for

water splitting (Tang *et al.*, 2016; Gaillard *et al.*, 2013) and photocatalyst (Yourey, 2014). The preparation of CuWO_4 plays vital role in determining the supercapacitance. Hydrothermal synthesis (Yang *et al.*, 2013) of metal oxides is a promising method for large scale and low-cost production with high-quality crystals. Recently many works have been reported on graphene based metal oxides (Liu *et al.*, 2010b; Wang *et al.*, 2015; Dong *et al.*, 2012; Huang *et al.*, 2012) to enhance the performance of supercapacitor because graphene shows (Geim, 2009) large surface area, high electrical conductivity (Neto *et al.*, 2009), thermal conductivity (Balandin, 2011), profuse interlayer structure and excellent mechanical stability.

In this study we have reported the facile hydrothermal synthesis of CuWO_4 and CuWO_4 -reduced graphene oxide hybrid nanostructures. The morphology and composition have been characterized using XRD, SEM and EDAX. The electrochemical measurements have been performed to study specific capacitance of the prepared materials.

Experimental Section

Chemicals Used

Copper (II) Sulphate anhydrous [CuO_4S , Alfa Aesar (India)], Urea [$\text{CH}_4\text{N}_2\text{O}$, SRL (India)], Sodium tungstate dihydrate [$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, Lobal Chemie (India)], Graphene Oxide [Reinste] were used to synthesize Copper Tungsten Oxide [CuWO_4] nanoparticles and CuWO_4 -reduced graphene oxide hybrid nanostructures. For electrochemical measurements 3M aqueous solution of potassium Hydroxide [KOH, 85%, Alfa Aesar (UK)] was used. All the chemicals were used as received without further variation.

Preparation of CuWO_4 and CuWO_4 -Reduced Graphene Oxide Hybrid Nanostructure

The synthesis of CuWO_4 and CuWO_4 -reduced graphene oxide hybrid nanostructures followed facile hydrothermal method. A mixture of 0.392 g CuO_4S , 0.79 g $\text{Na}_2\text{WO}_4 \cdot 2\text{N}_2\text{O}$ and 1.92 g urea was mixed in 40 mL of de-ionised water and stirred for 1 h at room temperature at 900 rpm. Then the solution was transferred to a 50 mL Teflon lined stainless steel autoclave and heated for 12 h at 200°C in hot air oven. After the synthesis, the precipitate was collected and rinsed several times with ethanol. Then the collected sample was dried at 70°C for and annealed at 450°C for 12 h.

For the synthesis of CuWO_4 -reduced graphene oxide hybrid nanostructures the same procedure has been followed as mentioned above but with addition graphene oxide to obtain different concentration of CuWO_4 -reduced graphene oxide hybrid nanostructures.

Material Characterization

The elemental composition and morphology of the prepared sample was investigated by Energy dispersive X-ray spectroscopy (EDAX) and Field Emission Scanning Electron Microscopy [(FESEM) (MERLIN Compact with GEMINI I electron column, Zeiss Pvt. Ltd., Germany)]. The powder X-ray diffraction spectra were measured by (Bruker D8 advanced diffractometer) method with $\text{Cu K}\alpha$ radiation, $\lambda = 0.154184$ nm. The electrochemical performance was recorded by a three electrode electrochemical test using a Potentiostat (PG-16125, Techno science instrument, Bangalore, India).

Preparation of Electrode and Electrochemical Measurement

The working electrode for electrochemical measurement was prepared by mixing the obtained sample with ethanol and then coating it on nickel foam. The prepared sample and ethanol was sonicated for almost 20 min to make homogeneous mixture and then coated on the rectangular nickel foam strip for two times to get uniform coating. Then the coated nickel foam was dried at room temperature in a vacuum container for almost 24 h followed by pressing. The mass of the Ni foam was recorded before the coating and after the coating to know the amount of material deposited on it. The electrochemical performance of the CuWO_4 and CuWO_4 -reduced graphene oxide hybrid nanostructures was observed by a three electrode electrochemical test using a Potentiostat (PG-16125, Techno science instrument, Bangalore, India) in 3M aqueous KOH solution. The Cyclic voltammetry and Charge-discharge tests were carried out at room temperature within a potential range between -0.1 to 0.4 V Vs. Ag/AgCl electrode. The coated nickel strip was used as the working electrode and Pt coil as counter electrode in this three electrode test. Specific capacitance (C_s) of a material is obtained from the cyclic voltammetry curve at different scan rates using the Equation 1:

$$C_s = \frac{\int_{V_i}^{V_f} I(V) dV}{m \cdot s \cdot [V_f - V_i]} \quad (1)$$

where, the numerator gives the total area under the CV curve, $[V_f - V_i]$ is called the potential window ($V_f =$ Final potential value and $V_i =$ Initial potential value), ' m ' is mass loaded on the Working electrode and ' s ' is the scan rate.

The specific capacitance can also be obtained from the charge-discharge curve using Equation 2:

$$C_m = \frac{I}{m \cdot \frac{dV}{dt}} \quad (2)$$

where, ' I ' is the discharge current, ' m ' is the mass of sample loaded on the working electrode and ' dV/dt ' is the slope of the discharge curve.

Results and Discussion

Composition and Morphology Study

Figure 2(a) and (b) shows the FESEM picture of CuWO_4 -reduced graphene oxide hybrid nanostructures. From the image it can be clearly observed that the prepared sample consists of nanoparticles of avg. diameter 20-30 nm. The uniform growth of the 80 mg CuWO_4 -reduced graphene oxide hybrid nanostructures nanoparticle was examined from the Fig. 2(c) shows the EDAX spectrum and elemental composition data which demonstrates the presence of Cu, W, O and C that confirms the proper formation of CuWO_4 -reduced graphene oxide hybrid nanoparticles. For further understanding of chemical

composition of the prepared sample the elemental mapping is studied which is shown in Fig. 3.

X-Ray Diffraction

Figure 1 shows the X-ray diffraction peaks of the CuWO_4 -reduced graphene oxide hybrid nanostructures and CuWO_4 . The peak matches completely with the characteristic peaks of CuWO_4 (Jcpds No 88-0269). In addition to the characteristic peaks of CuWO_4 , the peaks of graphene can be observed from the figure. The peak at $2\theta = 25.95^\circ$ can be interpreted as the merged peak of CuWO_4 [(110)] and graphene [(111)]. The characteristic peaks of graphene shows two peaks at $2\theta = 26.5^\circ$ (111) and 54.6° (222). Here, in figure two peaks were observed due to the presence of graphene one at $2\theta = 25.95^\circ$ and the other at 55° . The combined presence of both CuWO_4 and graphene confirms the formation of pure CuWO_4 -reduced graphene oxide hybrid nanostructures.

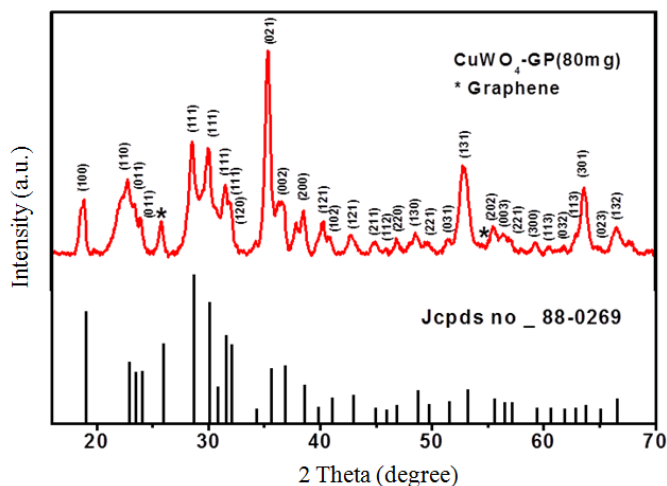


Fig. 1. X-ray diffraction of CuWO_4 -reduced graphene oxide hybrid nanostructures and comparison with JCPDS file No-88-0269

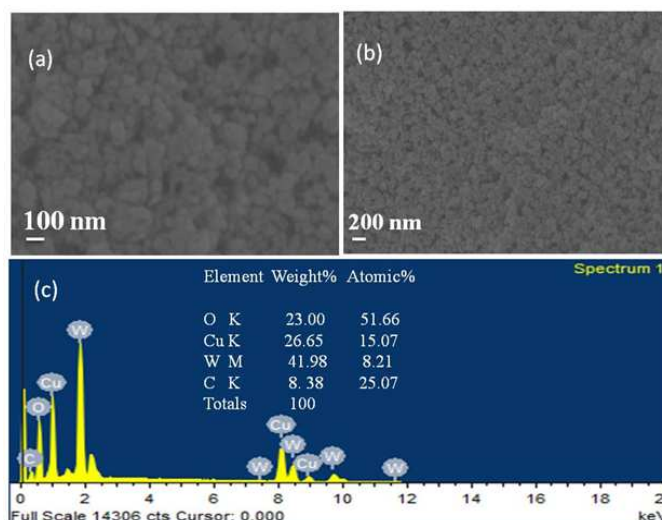


Fig. 2. (a) High magnification (b) Low magnification FESEM images (c) EDS spectra showing composition of constituent elements Cu, W, O, C

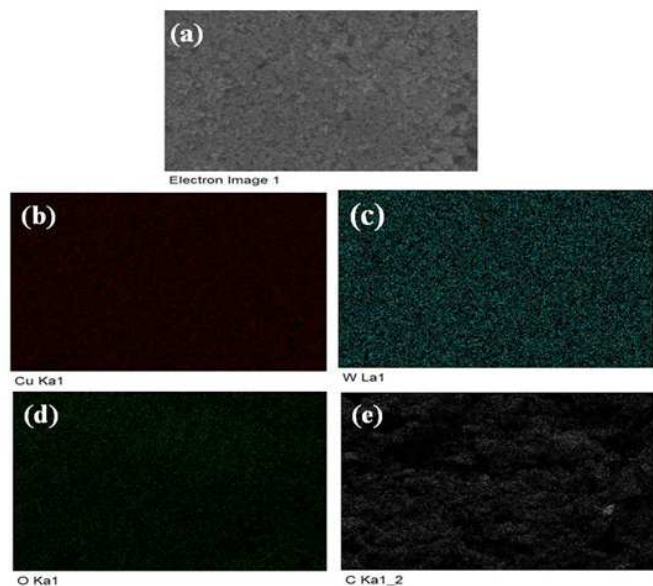


Fig. 3. Elemental mapping of CuWO₄-reduced graphene oxide hybrid nanostructures (a) electronic image over which mapping has been performed (b) presence of Cu (c) presence of W (d) presence of O (e) and presence of C is confirmed from the mapping data

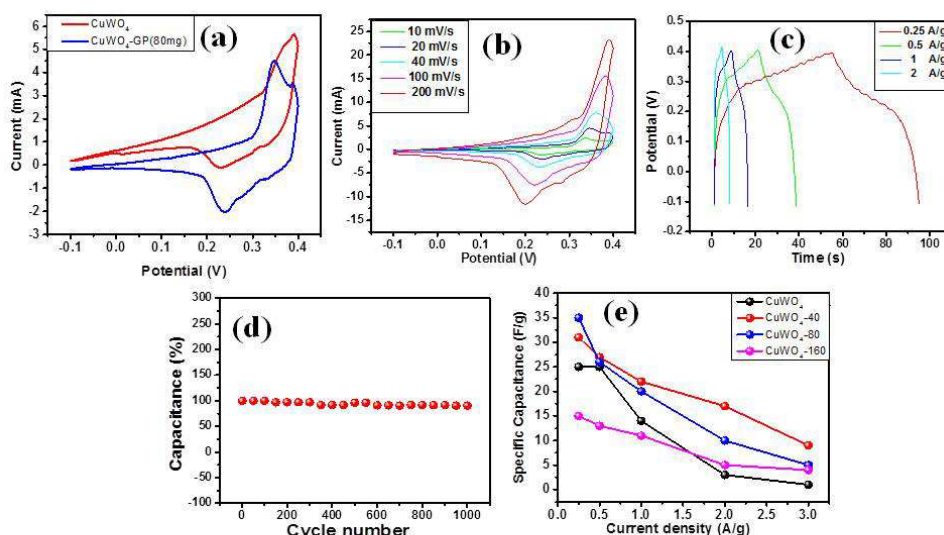


Fig. 4. Electrochemical study of CuWO₄-reduced graphene oxide hybrid nanostructures (a) CV curves comparing CuWO₄ and 80 mg CuWO₄-reduced graphene oxide hybrid nanostructures (b) CV curves of 80 mg CuWO₄-reduced graphene oxide hybrid nanostructures CuWO₄ at different scan rates (c) CD curves of 80 mg CuWO₄-reduced graphene oxide hybrid nanostructures at different current densities (d) Cycle Number vs. percentage of capacity retention of the 80 mg CuWO₄-reduced graphene oxide hybrid nanostructures CuWO₄ showing good stability over 1000 cycles (e) Current Density vs. specific capacitance curves of different synthesized materials

Electrochemical Measurement

The electrochemical measurements were carried out to study the supercapacitive behavior of the synthesized materials. The measurements followed three electrode cyclic voltammetry and charge discharge test in 3M aqueous KOH solution. The experiments were performed keeping the potential window in the range of -

0.1 to 0.4 volt. Figure 4(a) shows the cyclic voltammetry measurement of CuWO₄ and 80 mg CuWO₄-reduced graphene oxide hybrid nanostructures. From this figure it was calculated that CuWO₄ shows specific capacitance (Cs) of 11.8 F/g while 80 mg CuWO₄-reduced graphene oxide hybrid nanostructures shows specific capacitance (Cs) of 16.6 F/g at 2 mv/s scan rate. The cyclic voltammetry curves of 80 mg CuWO₄-reduced graphene

oxide hybrid nanostructures at different scan rates can be examined from the Fig. 4(b). It can be observed that the decrease of specific capacitance and shifting of the reduction peak towards left takes place with increase in scan rate. The maximum obtained specific capacitance of the 80 mg CuWO₄-reduced graphene oxide hybrid nanostructures was found to be 16.6 F/g at 2 mv/s. The galvanostatic charge discharge test was conducted to have better understanding of the supercapacitive performance of the material. Figure 4(c) shows the charge-discharge curves of the 80 mg CuWO₄-reduced graphene oxide hybrid nanostructures at different current densities of 0.25, 0.5, 1 and 2 A/g. The maximum value of specific capacitance from charge discharge curves was found to be 35.71 F/g at current density of 0.25 A/g. Here the specific capacitance decreases with increase in current density which can be clearly observed from the figure. From the Fig. 4(d) the cycle stability of the 80 mg CuWO₄-reduced graphene oxide hybrid nanostructures CuWO₄ can be clearly observed. The long Cycle stability is the most important criteria for a material to perform as supercapacitor. Here, from the figure it can be inferred that the CuWO₄-reduced graphene oxide hybrid nanostructures material shows good cycle stability over 1000 cycles. The galvanostatic charge discharge test for cycle stability was performed at 10 A/g. The material has maintained the initially obtained specific capacitance value even at 1000 cycles. This ensures the material to be a promising candidate for supercapacitor application. Figure 4(e) shows a comparison curve of different synthesized materials on the basis of their specific capacitance value. The different synthesized materials are CuWO₄, 40 mg CuWO₄-reduced graphene oxide hybrid nanostructures, 80mg CuWO₄-reduced graphene oxide hybrid nanostructures and 160 mg CuWO₄-reduced graphene oxide hybrid nanostructures. From the charge discharge curve it was calculated that the synthesized material shows specific capacitance of 25, 31.2, 35.7 and 15.6 at 0.25 A/g respectively. Hence, the 80 mg CuWO₄-reduced graphene oxide hybrid nanostructures shows highest specific capacitance of 35.7 F/g with excellent cycle stability and can be utilized as a promising electrode for supercapacitor application in future.

Conclusion

Here we report the successful synthesis of CuWO₄ and CuWO₄-reduced graphene oxide hybrid nanostructures by hydrothermal route. The XRD, FESEM, EDAX illustrates the morphology and structure of the prepared sample in detail. The supercapacitive behavior has been studied using cyclic voltammetry and galvanostatic charge discharge tests. Among all prepared samples the CuWO₄-reduced graphene oxide hybrid nanostructures shows maximum specific capacitance of 35.71 at 0.25 A/g with excellent cycle stability. Considering all the obtained data, the

CuWO₄-reduced graphene oxide (with 80 mg GO) hybrid nanostructures can be utilized as an electrode for supercapacitor application.

Funding Information

Dr. C.S. Rout would like to thank DST (Government of India) for the Ramanujan fellowship. This work was supported by the DST-SERB Fast-track Young scientist (Grant No. SB/FTP/PS-065/2013), Ramanujan Fellowship research grants (Grant No. SR/S2/RJN-21/2012) and UGC-UKIERI thematic awards (Grant No. UGC-2013-14/005).

Author's Contributions

All the authors contributed equally.

Ethics

The authors declare no competing financial interest. This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

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