International Journal of Pioneering Technology and Engineering

Research Article

New Approach for Preparation of Bi_2O_3-Carbon Nanotube Composites Using Celestine Blue Dispersant with High Mass Loading

Mustafa Sami Ata[a*]

[a] Department of Mechanical Engineering, Engineering Faculty, Amasya University, Amasya, Turkey

Article Info

Article history
Received: 15.05.2022
Revised: 31.05.2022
Accepted: 06.06.2022

Keywords:
Bismuth oxide,
Carbon nanotubes,
Composites,
Supercapacitor

ABSTRACT

This paper focused on to prepare Bi_2O_3-multiwalled carbon nanotube (MWCNT) nanocomposites electrodes for supercapacitor applications with high mass loading. Nature inspired dispersing agent Celestine blue (CB), different adsorption mechanism in different materials, dispersed MWCNT and Bi_2O_3 and allowed to prepare homogenous electrode with high mass loading on a porous NiFoam current collector. The areal capacitance of 555 mF cm^{-2} was obtained from the composite electrode with 25 mg cm^{-2} active mass loading in 1M Na_2SO_4 electrolyte. Bi_2O_3/MWCNT/CB composited electrode testing results showed promising results for supercapacitor applications.

1. Introduction

With increasing energy demand and limited fossil fuels, also the increase in environmental awareness generates a need for other energy sources and energy storage searches. For the last couple of decades, supercapacitors (SCs) have been widely attractive worldwide because of their long cycle life (>105), low maintenance, fast charge/discharge and most importantly high-power density over the conventional batteries [1–3]. Yet, the disadvantage of SCs is their low energy density, which is one of the biggest drawbacks of this energy storage system [1]. Based on the energy storage mechanisms, SCs can be divided into two types: (i) carbon-based electrode electrical double layer capacitor (EDLC) and (ii) metal oxide and conducting polymer-based electrodes pseudocapacitors. Hybrid mechanism, the combination of Faradaic type electrodes with pseudocapacitive and non-Faradaic carbon electrodes with EDLC charge storage mechanism has been widely investigated.

Pseudocapacitive materials, such as MnO_2[4-5], Co_3O4[6], NiO[7], Fe_3O4[8], and ZnO[9] have been widely studied as positive electrode materials for SCs application. On the other hand, there is not too much research on the cathode electrode material performance. Bi_2O_3 and Fe_2O_3 showed promising result; however, low specific capacitance, poor rate capability and cyclic stability have to be overcome [10–12].

The advantage of Bi-based electrode is high semiconductor band gap (Eg, of 2.85 eV for α-Bi_2O_3) high dielectric permittivity and high oxygen conductivity [13].

The goal of this investigation was to prepare Bi_2O_3 electrode with multiwalled carbon nanotube (MWCNT) with celestine blue as a dispersant agent for SCs applications to overcome their disadvantages. Celestine blue (CB) was used as a dispersing agent for colloidal fabrication of Bi_2O_3-MWCNT. The possibility of Bi_2O_3 and MWCNT dispersion with using CB as a dispersing agent paves the way for further investigations in the future.

2. Experimental procedures

Celestine blue (CB), Bismuth (III) Nitrate, citric acid (CA), nitric acid, potassium hydroxide (KOH), poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (PVB, average Mw = 50,000–80,000) and MWCNT (inner and outer diameter 6 and 13 nm) were purchased from Sigma Aldrich. As a current collector, Ni foam was used with 95% porosity provided by Vale Limited Company.

The synthesis of Bi_2O_3 particles were prepared as follows. Firstly, 0.97 g Bismuth (III) nitrate and 0.13 g citric acid were dissolved in 40 ml of nitric acid (1M). Then, potassium hydroxide solution (KOH, 8M) added dropwise until the pH value was 6. After 10 min well mixing, the solution was transferred into a Teflon-lined stainless-steel autoclave to

*Corresponding author: Mustafa Sami Ata
*E-mail address: mustafa.ata@amasya.edu.tr
https://doi.org/10.56158/jpte.2022.25.1.01

perform a hydrothermal process at 200 °C for 12 h. Then, the solid product was centrifuged, washed with deionized water and absolute alcohol for several times to remove any remaining impurities and dried at 60 °C for further characterization. For the final step, calcination process is applied at 400 ºC for 3h to prepare yellowish Bi_2O_3 powder[14].

1 gL^{-1} MWCNT was dispersed in the Celestine blue solutions, containing 0.5 gL^{-1}. The prepared suspension ultrasonicated for 30 min. Then, 4 gL^{-1} of Bi_2O_3 powder was added into the suspension. The obtained mixture was filtrated, washed and dried in air. 2% PVB by the weight of the total composite mass added with ethanol solution. The prepared slurry impregnated to Ni foam collector and fabricated 1 cm^2 area with an active mass loading was 27 mg cm^{-2} (±10%).

The morphology information of the samples was investigated by scanning electron microscopy (FEI NOVANANOSEM 650). Thermo Scientific Nicolet iS10 and PANALYTICA EMPYREAN were used for the crystallographic investigation of FT-IR and XRD analysis, respectively. Gamry Reference 3000 was used for cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The capacitive behavior of the single electrode was investigated in three-electrode cell using 1 M Na_2SO_4 aqueous solution. The counter electrode was graphite pencil (0.0244 cm^2) and reference electrode was standard saturated calomel electrode (SCE). CV studies were performed at a scan rate of 2–100 mVs^{-1}. The specific capacitance of the CV was calculated as following Equation 1;

$$Cs=A/(2S(dV/dt)\Delta V) \quad (1)$$

where Cs (Fcm^{-2}) is the gravimetric specific capacitance. A/2 is the integrated area of the calculated from CV curve, S (cm^2) is electrode area (or mass (m) (g)), dV/dt is scan rate (mV s^{-1}) and ΔV is potential of the of the CV curve.

3. Results and discussion

Bi_2O_3 is a promising cathode material for supercapacitor applications. However, it is very difficult to observe good performance especially at high active mass loading. Another challenge is Bi_2O_3 have to very well mixed with dispersed MWCNT. Both materials are very prone to agglomerate by themselves.

A schematic of the chemical structure of CB, which has aromatic rings, hydrocarbon chains and catechol-type families (Figure 1). The aromatic rings are critical for MWCNT, which adsorption mechanism depends on the π-π interaction. Another bonding mechanism is catechol-type bonding includes strong mussel's protein adsorption on any surface. With this mechanism, electrostatic interactions are involved between Bi_2O_3 and CB.

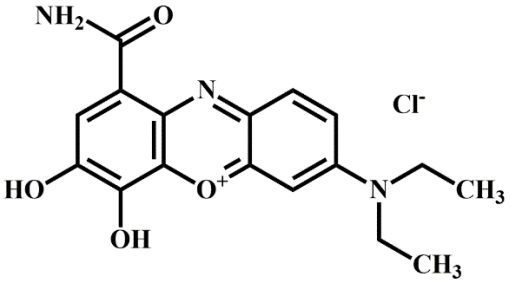

Fig.1 Schematic of the chemical *structure* of CB

In this paper, MWCNTs and Bi_2O_3 were dispersed separately, and CB was included in each solution. After half an hour of stirring and ultrasonication process, two solutions were mixed and kept under ultrasonication for another 30 min. The SEM image illustrated below for as obtained Bi_2O_3 and Bi_2O_3-MWCNT-CB showed Bi_2O_3/MWCNT/CB well mixed and attached perfectly with each other (Figure 2 A and B).

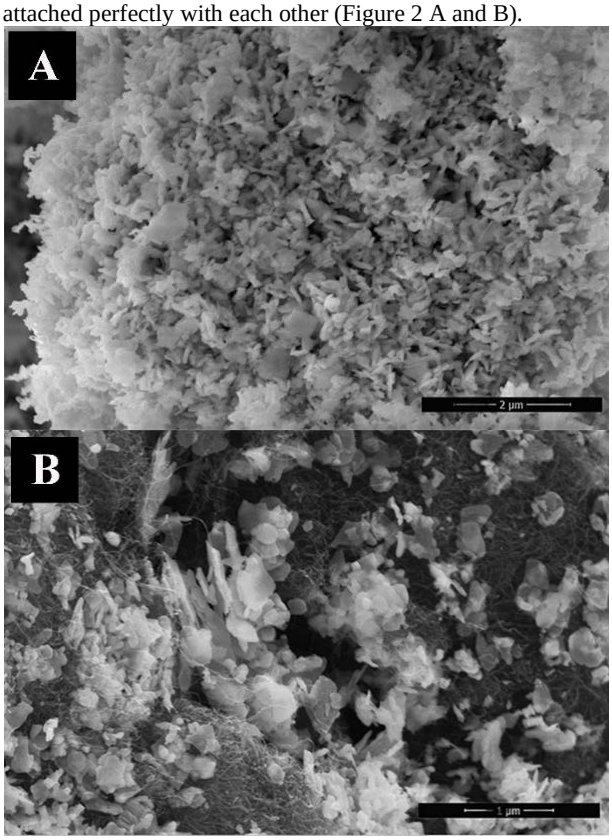

Fig. 2 SEM images of A)pure Bi_2O_3 and B)Bi_2O_3-MWCNT-CB mixture

The use of CB in the mixture significantly increased the electrochemical performance (Figure 3 A). The single electrode cyclic voltammetry test of the composite electrode was examined in 1 M Na_2SO_4 solution. The composite Bi_2O_3-MWCNT electrode was prepared using CB as a co-dispersing agent. CV curves at different scan rates were nearly box shaped which indicates good electrochemical performance and obvious pseudocapacitance performance with two Faradaic redox reaction peaks. These peaks are indicated with the Na+ ion extraction and insertation and explained below by the following Equaition 2 [15-16]:

$$Bi_2O_3 + xNa^+ + xe^- \longleftrightarrow Na_xBi_2O_3 \quad (2)$$

It is important to note that the specific capacitance, calculated from integrated CV curves in a voltage window 0.9 V (-0.9 to 0 V). The specific capacitance decreased from 555 mF cm^{-2} to 110 mF cm^{-2} with increasing the scan rate from 2 to 100 mVs^{-1} for 25 mg cm^{-2} active mass loading. Conversely, pure Bi_2O_3 electrode CV test result was only 125 mF cm^{-2} at 2 mVs^{-1} which was 4 times lower than composite electrode (Figure 3 B). The composite electrode exhibited lower resistance compared to the pure Bi_2O_3 electrode (Figure 3 C). The Bode plots of real and imaginary parts of Bi_2O_3/MWCNT/CB composite electrodes, respectively (Figure 3 D). The capacitance derived from the CVs at relatively low scan rates was comparable with real part of capacitance, derived from the electrochemical complex impedance data in the low frequency range [17].

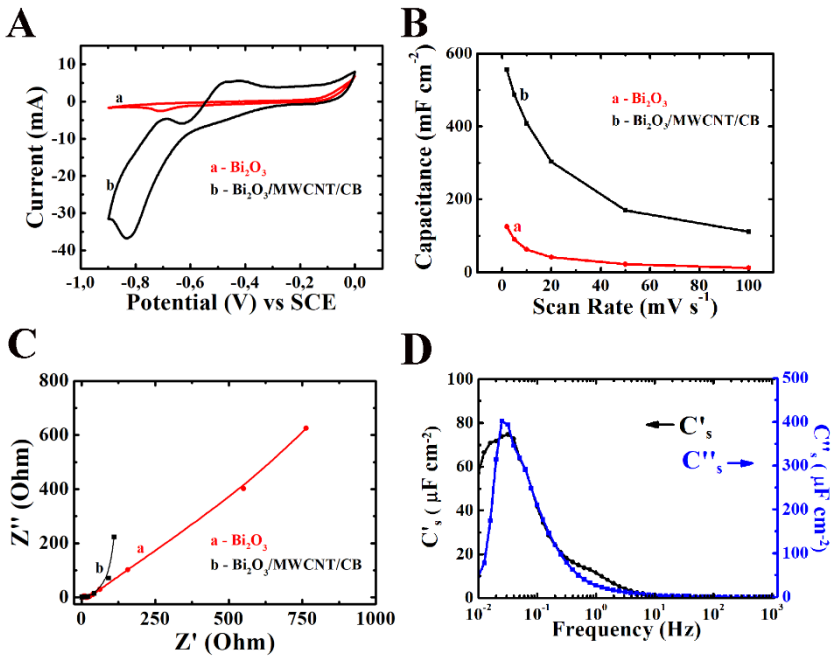

Fig. 3 (A) CVs at scan rate 10 mV s^{-1}, (B) Nyquist plot and (C) Specific areal capacitance of (a) Bi_2O_3 and (b) Bi_2O_3/MWCNT/CB composites, (D) real part C'$_s$ and imaginary part C''$_s$ of capacitance, calculated from the impedance data for Bi_2O_3/MWCNT/CB composite.

4. Conclusion

Bi_2O_3 and Bi_2O_3/MWCNT/CB composite electrodes were synthesized, and electrode materials were prepared for supercapacitors application test. SEM analysis proved that the composite mixture very well mixed, and homogenous electrode surface was achieved. The adsorption of CB on Bi_2O_3 and MWCNT strongly established. A good specific capacitance of 555 $mFcm^{-2}$, at a high mass loading of 25 mg cm^{-2} as active material in 1M Na_2SO_4 electrolyte, showed promising results for the future investigation. Compared to the pure Bi_2O_3 electrode, results have increased by 4 times.

Declaration of conflicting interests

The authors declared no conflicts of interest with respect to the authorship and/or publication of this article.

Acknowledgment

The author acknowledges to Doç. Dr. Yaşar Özkan YEŞİLBAĞ at Erzincan University, Faculty of Arts and Science, Department of Physics and Dr. Erhan KARACA at Hacettepe University, Faculty of Science, Department of Chemistry for their valuable support.

Funding

This research was supported by Scientific Research Project (BAP no: FMB-BAP 19-0392), funded by Amasya University, Türkiye.

References

[1] P. Simon and Y. Gogotsi, "Materials for electrochemical capacitors," *Nat. Mater.*, vol. 7, p. 845, Nov. 2008.

[2] Z. S. Iro, "A Brief Review on Electrode Materials for Supercapacitor," *Int. J. Electrochem. Sci.*, pp. 10628–10643, Dec. 2016.

[3] G. Wang, L. Zhang, and J. Zhang, "A review of electrode materials for electrochemical supercapacitors," *Chem. Soc. Rev.*, vol. 41, no. 2, pp. 797–828, 2012.

[4] M. S. Ata, S. Ghosh, and I. Zhitomirsky, "Electrostatic assembly of composite supercapacitor electrodes, triggered by charged dispersants," *J. Mater. Chem. A*, vol. 4, no. 45, pp. 17857–17865, 2016.

[5] H. Zhou and Y. Zhang, "Enhanced electrochemical performance of manganese dioxide spheres deposited on a titanium dioxide nanotube arrays substrate," *J. Power Sources*, vol. 272, pp. 866–879, 2014.

[6] Y. Wang, Y. Lei, J. Li, L. Gu, H. Yuan, and D. Xiao, "Synthesis of 3D-Nanonet Hollow Structured Co3O4 for High Capacity Supercapacitor," *ACS Appl. Mater. Interfaces*, vol. 6, no. 9, pp. 6739–6747, May 2014.

[7] R. S. Kate, S. A. Khalate, and R. J. Deokate, "Overview of nanostructured metal oxides and pure nickel oxide (NiO) electrodes for supercapacitors: A review," *J. Alloys Compd.*, vol. 734, pp. 89–111, 2018.

[8] M. Nawwar, R. Poon, R. Chen, R. P. Sahu, I. K. Puri, and I. Zhitomirsky, "High areal capacitance of Fe3O4-decorated carbon nanotubes for supercapacitor electrodes," *Carbon Energy*, vol. 1, no. 1, pp. 124–133, Sep. 2019.

[9] A. Darari, I. S. Hakim, Priyono, A. Subagio, Pardoyo, and A. Subhan, "The effect of temperature deposited on the performance of ZnO-CNT-graphite for supercapacitors," *J. Phys. Conf. Ser.*, vol. 877, p. 12006, 2017.

[10] J. Ma, X. Guo, Y. Yan, H. Xue, and H. Pang, "FeOx-Based Materials for Electrochemical Energy Storage," *Adv. Sci.*, vol. 5, no. 6, p. 1700986, Jun. 2018.

[11] H. Xu, X. Hu, H. Yang, Y. Sun, C. Hu, and Y. Huang, "Flexible Asymmetric Micro-Supercapacitors Based on Bi2O3 and MnO2 Nanoflowers: Larger Areal Mass Promises Higher Energy Density," *Adv. Energy Mater.*, vol. 5, no. 6, p. 1401882, Mar. 2015.

[12] Y. Zeng, M. Yu, Y. Meng, P. Fang, X. Lu, and Y. Tong, "Iron-Based Supercapacitor Electrodes: Advances and Challenges," *Adv. Energy Mater.*, vol. 6, no. 24, p. 1601053, Dec. 2016.

[13] Y. Qiu, D. Liu, J. Yang, and S. Yang, "Controlled Synthesis of Bismuth Oxide Nanowires by an Oxidative Metal Vapor Transport Deposition Technique," *Adv. Mater.*, vol. 18, no. 19, pp. 2604–2608, Oct. 2006.

[14] L. Zhang, Y. Hashimoto, T. Taishi, I. Nakamura, and Q.-Q. Ni, "Fabrication of flower-shaped Bi2O3 superstructure by a facile template-free process," *Appl. Surf. Sci.*, vol. 257, no. 15, pp. 6577–6582, 2011.

[15] A. Deepi, G. Srikesh, and A. S. Nesaraj, "Electrochemical performance of Bi2O3 decorated graphene nano composites for supercapacitor applications," *Nano-Structures & Nano-Objects*,

vol. 15, pp. 10–16, 2018.

[16] Xu, H., Hu, X., Yang, H., Sun, Y., Hu, C., Huang, Y.. Flexible Asymmetric Micro-Supercapacitors Based on Bi2O3 and MnO2 Nanoflowers: Larger Areal Mass Promises Higher Energy Density. Adv. Energy Mater., 5: 1401882.2015.

[17] M. S. Ata & I. Zhitomirsky (2016) Electrochemical Deposition of Composites Using Deoxycholic Acid Dispersant, Materials and Manufacturing Processes, 31:1, 67-73.