Int. J. Nano Dimens., 11 (1): 26-31, Winter 2020

ORIGINAL ARTICLE

Tetrabutylammonium Perchlorate electrolyte on electrochemical properties of spinel $MgCo_2O_4$ nanoparticles

Saranya Arumugam [1], Soundhirarajan Perumal [2], Gohulkumar Muthusamy [1], Silambarasan Murugesan [1,*], Kandiban Ganesan [1]

[1] *Vivekanandha College of Arts and Sciences for Women (Autonomous), Tiruchengode, Tamilnadu 637205, India*

[2] *St. Joseph University, Ikishe Model Village, Dimapur, Nagaland 797115, India*

Received 20 October 2019; revised 04 December 2019; accepted 05 December 2019; available online 05 December 2019

Abstract

Spinel magnesium Cobaltite ($MgCo_2O_4$) nanoparticles with a crystalline size in the range of ~16 nm were prepared by a simple co-precipitation technique with NaOH as a precipitant. The formation of spinel $MgCo_2O_4$ phase was confirmed by X-ray diffraction (XRD) pattern. Scanning electron microscope (SEM) images showed that aggregated nanoplates. The electrochemical performance of modified $MgCo_2O_4$ electrodes was investigated with 2M of tetrabutylammonium perchlorate (TBA) electrolyte. The cyclic voltammetry (CV) results revealed that the $MgCo_2O_4$ electrode reached the highest specific capacitance of 390 °F/g at a scan rate of 5mV/s. The excellent electrochemical performance was absorbed due to the electrochemical faradaic redox reactions related to the intercalation/de-intercalation of the tetrabutylammonium cation (TBA^+) and $MgCo_2O_4$ lattice, and brings an additional pseudocapacitive contribution. The present work proves that the prepared magnesium cobaltite can serve as advanced electrode material for next generation organic electrolyte supercapacitors.

Keywords: *Electrode; Electrolyte; Magnesium Cobaltite; Specific Capacitance; Supercapacitor.*

How to cite this article

Arumugam A, Perumal S, Muthusamy G, Murugesan S, Ganesan K. Tetrabutylammonium Perchlorate electrolyte on electrochemical properties of spinel $MgCo_2O_4$ nanoparticles. Int. J. Nano Dimens., 2020; 11 (1): 26-31.

INTRODUCTION

The nanoscale materials are significant in the fields of advanced research because of their outstanding physico-chemical properties. Specifically, binary metal oxides have attracted the scientific community due to their potential applications in energy storage devices such as li-ion battery, supercapacitor, etc [1, 2]. Currently, spinel (AB_2O_4) type of binary metal oxide has broadly explored as an electrode materials for the application of supercapacitors due to their mixed spinel structure and potential oxidation state. Cobalt-containing spinel binary oxides, such as $ZnCo_2O_4$, $CuCo_2O_4$, $NiCo_2O_4$, $MnCo_2O_4$ and $MgCo_2O_4$ [3-8] are technologically fascinating materials and have been utilized as electrode materials for electrochemical capacitor application. Among them, spinel type magnesium cobaltite ($MgCo_2O_4$) is an intriguing candidate for anode material in Li-ion batteries, which have high theoretical capacitance than those of the cobalt based oxides family [9]. $MgCo_2O_4$ materials have a stable structure and theoretical specific capacitance in the range of 3122 F g^{-1} [10]. To the best of our knowledge, there are only few works reported on $MgCo_2O_4$ nanoparticles for supercapacitors. In our previous work, we reported on one dimensional $MgCo_2O_4$ nanostructures for supercapacitor, which exposed a good specific capacitance in the range of 752 F g^{-1} in aqueous electrolyte [8]. L. Cui et al., have reported $MgCo_2O_4$ nanocone arrays grown on three-dimensional nickel foams and practical specific capacitance in the range of ~750 F g^{-1} was achieved in KOH solution as electrolyte [9]. Most of the peer researchers have been carried out through aqueous electrolytes

* Corresponding Author Email: *silambanphy@gmail.com*

This work is licensed under the Creative Commons Attribution 4.0 International License.
To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

owing to their low ionic resistivity and which have lower operating potential, related to the problems of oxygen and hydrogen evolution reaction. Most commonly, organic electrolytes are used instead of aqueous electrolytes due to their higher operating potential (2.5V), which is highly desirable for high-energy-density supercapacitors [11]. More importantly, no effort has been taken so far to study the electrochemical properties of $MgCo_2O_4$ nanoparticles in tetrabutylammonium perchlorate (TBA) electrolyte. Based on this consideration, we have synthesized $MgCo_2O_4$ nanoparticles via simple co-precipitation method and characterized their electrochemical properties in tetrabutylammonium per chlorate (TBA) electrolyte solution for supercapacitor application.

MATERIALS AND METHODS

Preparation of $MgCo_2O_4$ nanoparticles

The synthesis of magnesium cobaltite nanostructure was prepared from $Mg(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ as precursors. For the preparation of $MgCo_2O_4$, 1 mM of $Mg(NO_3)_2{\cdot}6H_2O$ and 2 mM of $Co(NO_3)_2{\cdot}6H_2O$ precursors were dissolved carefully in 50 ml of de-ionized water to form homogeneous solution. 3mM of NaOH as precipitant was slowly dropped into the above solution under constant magnetic agitation for 30 min. The mixture of solution was transferred into a 250 ml conical flask and heated to 80°C in an oil bath with constant magnetic stirring for 5 h. The obtained precipitate was washed by milli-Q water and ethanol several times to remove the impurities. Then the product was dried at 60 °C for 8h under vacuum condition, finally the powder was calcinated at 400°C for 4 h to obtain $MgCo_2O_4$ nanoparticles.

Electrochemical characterization

The electrochemical properties of $MgCo_2O_4$ modified glassy carbon electrode (GCE) were carried out by electrochemical workstation (CHI 660C, USA). A bare GCE was cleaned and rinsed with de-ionized water. The electrode material of $MgCo_2O_4$ (1.55 mg ml^{-1}) were dispersed in an aqueous solution of ethanol to form slurry. The obtained slurry sonicated for 10 min. Then 20 µl of slurry was placed onto the GCE surface using a micropipette. After the solvent was evaporated, the electrode surface was covered with 5 ml of Nafion solution, and the electrodes were dried at 70 °C for 1 h under vacuum to evaporate the solvent. The modified magnesium cobaltite as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire act as the counter electrode, respectively. The area of the working electrode immersed into the electrolyte solution was controlled to be about approximately 1.5 cm^2. Typical cyclic voltammetry tests were carried out with the potential window from −1.5 to 1.8 V (vs. SCE) with different scan rates varying from 5 to 50 mV/s at room temperature. Electrochemical measurements were carried out in 2M Tetrabutylammonium perchlorate (TBA) with a standard three electrode configuration consisting of a sample (working electrode), an Ag/AgCl (reference electrode) and a high platinum wire (counter electrode).

The specific capacitances of the modified electrodes were calculated from cyclic voltammograms with the help of following equation [12].

$$Cs = \frac{Q}{\Delta v.m} \quad (1)$$

Where *Cs* represents the specific capacitance, *Q* the anodic and cathodic charges on each scanning, m is the mass of the electro active material (mg) and ΔV is the applied voltage window of the voltammetry curve (mVs^{-1}).

Characterization Techniques

All the characteristics were investigated carefully after calcination process. X-ray diffraction (XRD) pattern of the synthesized powder were recorded by Bruker-D8 ADVANCE using Cu Kα radiation. Scanning electron microscope (SEM) was characterized by FEI Quanta FEG 200 equipped with Energy dispersive X-ray analysis (EDAX). Transmission electron microscope (TEM) micrograph was obtained on a Philips CM10 with an accelerating voltage of 100 kV.

RESULTS AND DISCUSSION

Structural analysis

The X-ray diffraction (XRD) pattern of synthesized spinel $MgCo_2O_4$ using NaOH as precipitant was carried out to identify the presence of phase, crystallinity and purity of the sample, which is shows in Fig. 1. The diffraction peaks at 2θ = 19.03°, 31.27°, 36.84°, 38.65°, 44.73°, 55.74°, 59.32°, 65.25°, and 77.43°, which corresponds to (111), (220), (311), (222),

CC BY

(400), (422), (511),(440), and (533) hkl planes of spinel magnesium cobaltite respectively. All the diffraction peaks are well matched with standard card number (JCPDS card no. 81-0667). The sharp and intense diffraction peaks represent prepared sample is well crystalline nature. The crystalline size of the spinel magnesium cobaltite was determined in the range of 16 nm by scherrer formula [8]. No extra phases such as MgO and CO_3O_4 could be detected, which reveals that the prepared sample is composed of $MgCo_2O_4$ pure nanocrystals.

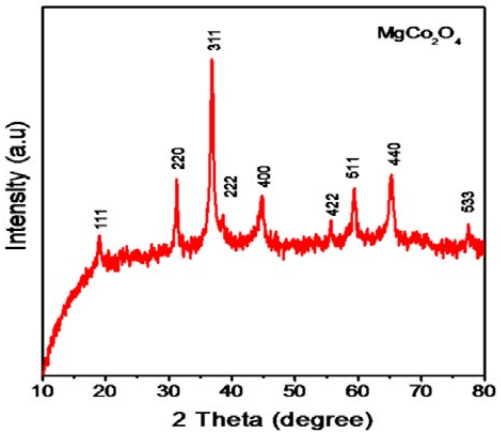

Fig. 1. The powder X-ray diffraction pattern of $MgCo_2O_4$.

Morphological Characterization

The surface morphology of the pure spinel $MgCo_2O_4$ nanocrystal image was carried out by different magnification of scanning electron microscope (SEM) as displayed in Fig. 2(a, b), respectively. The SEM images of $MgCo_2O_4$ show the inhomogeneous nanoplates and nanoparticles. Transmission electron microscope (TEM) images (Fig. 2c) confirms that the plate like nanostructure of $MgCo_2O_4$. SAED pattern of prepared materials are crystalline, which is shown in Fig. 2d. Energy dispersive X-ray analysis (EDAX) for the spinel $MgCo_2O_4$ sample is revealed in Fig. 3. The elements of the composition are confirmed from EDAX spectra, which indicates that the synthesized

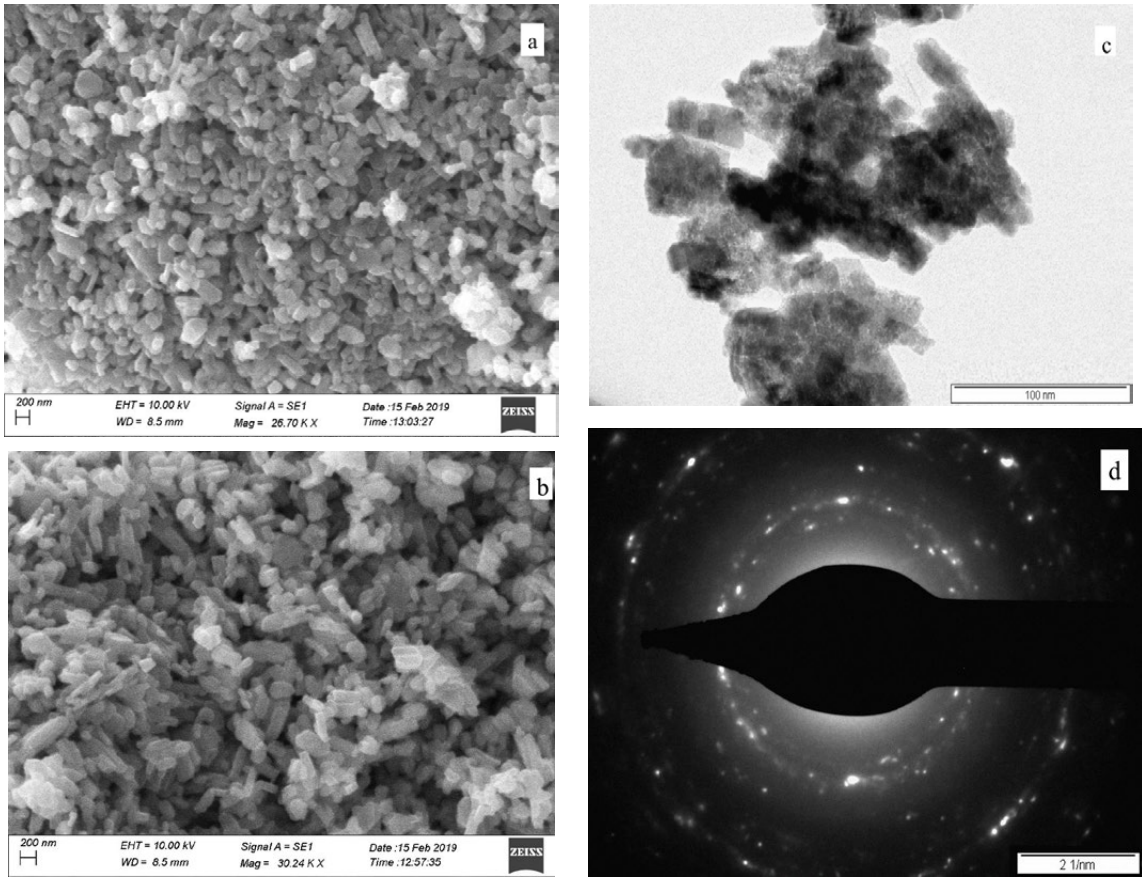

Fig. 2 (a, b). SEM images of as prepared sample (c) TEM image and (d) SAED pattern.

CC BY

nanoparticles do indeed consist of Mg, Co and O peaks with no other relevant element present. The analysis confirmed the formation of $MgCo_2O_4$ nanoparticles.

Electrochemical analysis of modified $MgCo_2O_4$. Cyclic voltammetry (CV) analysis

Cyclic voltammetry (CV) tests of modified electrodes were investigated under a conventional three-electrode cell with 0.2 M Tetrabutylammonium perchlorate electrolyte at different scan rates ranged from 5 to 50 mV/s are shown in Fig 4a. The organic electrolyte act as an alternative of an aqueous electrolyte, which is used to increase the operating potential reached window up to 1.8 V. The cyclic voltammetry curve of the magnesium cobaltite nanocrystals shows that the electrode deviates from idealized double-layer behaviors with reversible Faradic redox reactions, which indicates that the capacity of the material is mainly related with the pseudocapacitive properties [13, 14]. The specific capacitance of electrode material is directly proportional to the area of the cyclic voltammetry curve. From the cyclic voltammetry curves, the capacitance characteristics of the sample are mainly attributed to the electrochemical faradaic redox reactions related to the intercalation/de-intercalation of the tetrabutylammonium cation (TBA^+) into/ from $MgCo_2O_4$ lattice

$$MgCo_2O_4 + TBA^+ + e^- \rightarrow MgCo_2O_4(TBA)$$

In addition, the anodic and cathodic peak positions shift towards lower potential due to increasing of scan rate. The increase of the scan rate leads to the existence of the polarization [13].

The calculated specific capacitance values for the $MgCo_2O_4$ nanostructures are 390, 270, 195, 117, 80 and 33 F g^{-1} at the scan rate of 5, 10, 20, 30, 40 and 50 mV/s, respectively. The maximum specific capacitance of 390 F g^{-1} was obtained at a low sweep rate of 5 mV s^{-1}, which indicates the superior rate capability. The high specific capacitance of magnesium cobaltite could be attributed to the synergy effect between magnesium cobaltite and tetrabutylammonium perchlorate (TBA) electrolyte. The capacitance of the $MgCo_2O_4$ electrode gradually decreased with the increasing scan rate (Fig. 4b). At higher scan rates, the ionic diffusion takes place from the outer surface of the nanostructure, contributing little to the electrochemical capacitive behavior. At low scan rate, both inner and outer surfaces are responsible in the calibration of specific capacitance, and this corresponds to more ions adsorption and higher specific capacitance at low scan rate [15, 16]. The superior electrical properties of magnesium cobaltite electrode extend their potential applications in various self-powered wearable electronic devices.

CONCLUSION

In conclusion, we have successfully prepared magnesium cobaltite nanoparticles by simple co-precipitation method using NaOH as a precipitant. Then the prepared sample were

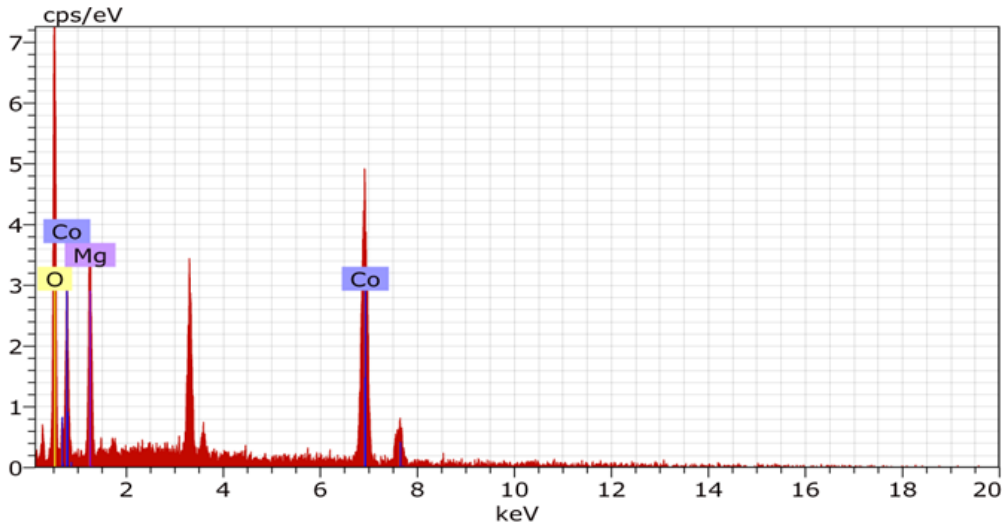

Fig. 3. EDAX analysis of $MgCo_2O_4$ nanoparticles.

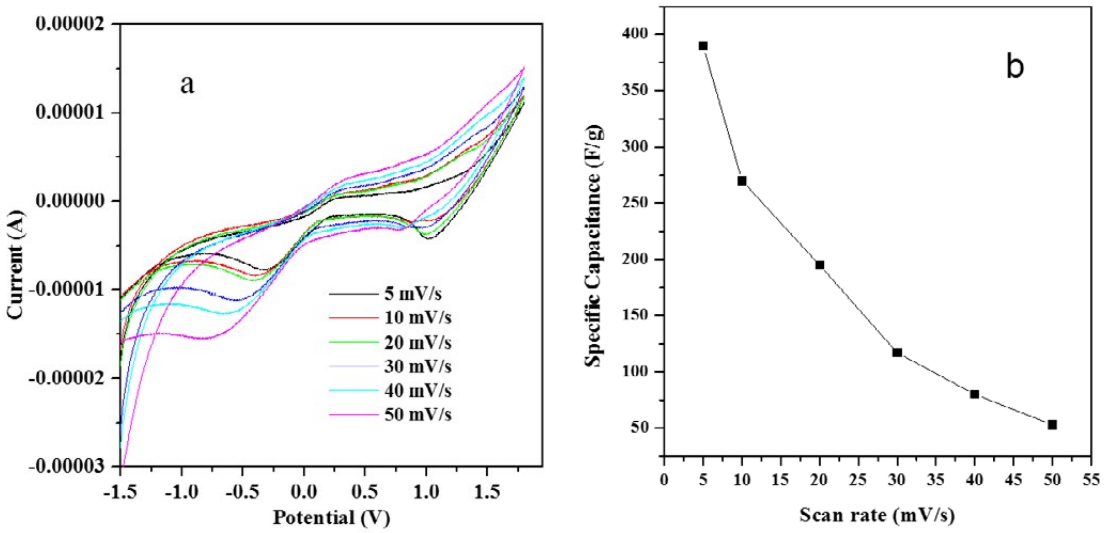

Fig. 4 (a, b). Cyclic voltammetry studies of the $MgCo_2O_4$ electrode.

characterized by X-ray diffraction (XRD), Scanning electron microscope (SEM)/Energy dispersive X-ray analysis (EDAX), Transmission electron microscope (TEM) and Cyclic Voltammetry (CV) respectively. The scanning electron microscope images show that the prepared nanoparticles exhibit aggregated nanoplates and nanoparticles images. When the spinel $MgCo_2O_4$ nanoparticles is used for electrochemical tests in at tetrabutylammonium perchlorate (TBA) electrolyte which exhibit pseudocapacitance performance with specific capacitance of 390 F/g at scan rate of 5mV/s. From the above discussion the spinel $MgCo_2O_4$ is a potential candidate for the application of organic electrolyte supercapacitor.

DISCLOSURE STATEMENT

All authors declare that they have no conflict of interest in the publication of this manuscript.

REFERENCES

1. Yufei Z., Laiquan L., Haiquan S., Wei H., Xiaochen D., (2015), Binary metal oxide: Advanced energy storage materials in supercapacitors. *J. Mater. Chem. A.* 3: 43-59.
2. Jun Y., Qian W., Tong W., Zhuangjun F., (2014), Recent advances in design and fabrication of electrochemical supercapacitors with high energy densities. *Adv. Energy Mater.* 4: 1300816-130019.
3. Silambarasan M., Ramesh P S., Geetha D., (2016), Facile one-step synthesis, structural, optical and electrochemical properties of $NiCo_2O_4$ nanostructures. *J. Mater. Sci. Mater. Electron*. 28: 323-336.
4. Wenbin F., Xiulei L., Changhui Z., Ying L., Peng Z., Jinyuan Z., Xiaojun P., Erqing X., (2015), Facile hydrothermal synthesis of flowerlike $ZnCo_2O_4$ microspheres as binder-free electrodes for supercapacitors. *Mater. Lett.* 149: 1–4.
5. Li L., Zhang Y. Q., Liu X. Y., Shi S. J., Zhao X. Y., Zhang H., Ge X., Cai G. F., Gu C. D., Wang X. L., Tu J. P., (2014), One-dimension $MnCo_2O_4$ nanowire arrays for electrochemical energy storage. *Electrochim. Acta*.116: 467–474.
6. Pendashteh A., Moosavifard S. E., Rahmanifar M. S., Wang Y., El-Kady M. F., Kaner R. B., Mousavi M. F., (2015), Highly ordered mesoporous $CuCo_2O_4$ nanowires, a promising solution for high-performance supercapacitors. *Chem. Mater.* 27: 3919–3926.
7. Silambarasan M., Padmanathan N., Ramesh P. S., Geetha D., (2016), Spinel $CuCo_2O_4$ anoparticles: facile one-step synthesis, optical, and electrochemical properties. *Mater. Res. Express.* 3: 095021-095025.
8. Silambarasan M., Ramesh P. S., Geetha D., Venkatachalam V., (2017), A report on 1D $MgCo_2O_4$ with enhanced structural, morphological and electrochemical properties. *J. Mater. Sci. Mater. Electron.* 29: 6880-6888.
9. Cui L., Huang L., Ji M., Wang Y., Shi H., Zuo Y., Kang S., (2016), High-performance $MgCo_2O_4$ nanocone arrays grown on three-dimensional nickel foams: Preparation and application as binder-free electrode for pseudo-supercapacitor. *J. Power Sources*. 333: 118–124.
10. Krishnan S. G., Reddy M. V., Harilal M., Vidyadharan B., Misnon I. I., Ab Rahim M. H., Ismail J., Jose R., (2015), Characterization of $MgCo_2O_4$ as an electrode for high performance supercapacitors. *Electrochim. Acta.* 161: 312–321.
11. Ce Y. F., Afriyanti S., Daniel J. H. T., Jiangxin W., Pooi

S. L., (2014), Flexible and highly scalable V_2O_5-rGO electrodes in an organic electrolyte for supercapacitor devices. *Adv. Energy Mater.* 4: 1400236-1400241.

12. Wu X., Meng L., Wang Q., Zhang W. Wang Y., (2017), A high performance asymmetric supercapacitor based on carbon fiber coated with $MgCo_2O_4$ nanobrush. *Mater. Lett.* 206: 71–74.
13. Sathishkumar K., Shanmugam N., Kannadasan N., Cholan S., Viruthagiri G., (2015), Synthesis and characterization of Cu^{2+} doped NiO electrode for supercapacitor application. *J. Sol–Gel Sci. Technol.* 74: 621-630.
14. Sathishkumar K., Shanmugam N., Kannadasan N., Cholan S., Viruthagiri G., (2015), Opto, magnetic and electrochemical characterization of $Ni_{1-x}Co_xO$ nanocrystals. *J. Mater. Sci. Mater. Electron.* 26: 1881-1889.
15. Gomaa A. M. A., Osama A. F., Salah A. M., Mashitah M. Y., Kwok F. C., (2014), Co_3O_4/SiO_2 nanocomposites for supercapacitor application. *J. Solid State Electrochem.* 18: 2505– 2512.
16. Gomaa A. M. A., Ling L. T., Rajan J., Mashitah M. Y., Kwok F. C., (2014), Electrochemical performance studies of MnO_2 nanoflowers recovered from spent battery. *Mater. Res. Bullet*. 60: 5–9.

CC BY