Chalcogenide Letters Vol. 17, No. 8, August 2020, p. 423 - 428

SYNTHESIS AND CHARACTERIZATION OF MoS_2 –GRAPENE OXIDE ON Ni-Co-MnO_2 NANOFIBER LIKE BINARY COMPOSITE FOR NICKEL FOAM BASED FLEXIBLE ELECTRODE FABRICATION

R. J. RAMALINGAM[a,*], H. AL-LOHEDAN[a,b], A. M. TAWFIK[a],
G. PERIYASAMY[b], M. R. MUTHUMAREESWARAN[c]
[a]*Surfactant Research Chair, Department of chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia*
[b]*Chemistry Department, College of Science, King Saud University, Riyadh 11451, Saudi Arabia*
[c]*King Abdullah Institute for Nanotechnology, College of Science, King Saud University, Riyadh 11451, Saudi Arabia*

Nickel/cobalt co-doped porous manganese oxide(MnOx) is fabricated by feasible non-ionic surfactant route followed by precipitation heat treatment method. The as prepared metal ion modified manganese oxide further impregnated *via* reducing graphene oxide and MoS_2 nanoparticles by ultra-sonication assisted deposition method. The as prepared binary nanocomposite is characterized by XRD and HR-TEM for crystalline phase formation analysis and structure morphology determination. Binder free flexible electrode fabrication on nickel foam using MoS_2/graphene modified Ni-Co-MnO_2 have also been studied and it shows higher super capacitor performance like 1190 F/g in aqueous acidic conditions.

(Received May 5, 2020; Accepted August 22, 2020)

Keywords: Composite materials, MoS_2, Manganese oxide, Graphene, Nanoparticles, Supercapacitor

1. Introduction

Porous manganese oxide is multivalent oxidation state and hence the foreign metal cation with suitable ionic radius or graphene like carbon compounds could deposit into lattice framework of mixed valent manganese oxide for improved electro catalytic performance [1,2]. It is necessary to develop electrode materials with low cost and efficient activity for the growing population all over the workd. Hence, the mangases oxide is one of the toxic less and low cost starting materials for sustainable development in the field of renewable energy applications [3,4]. Many different methods are already reported to prepare porous and mesoporous architechture of manganese oxide in the past few decades, includes to fabricate the nanoparticles of manganese oxide compoistes [5]. Wolfovich et al., (2005) developed cerium incorporated tunnel structured manganese oxide octahedral molecular sieves (OMS) by ion-exchange and wet impregnation method by low cost preparation routes for efficient phenol removal by catalytic wet oxidation [6]. The natural method to prepared the activated carbon from vairous bio-organic mateirals mixed with low cost metal oxide to prepare the hybrid nanomateirals is growing area of research. Recently, Xiao et al., fabricated manganese oxide with porous morphology coated on nitrogen intercalated carbon composite modifed electrode to imporved its pseudo capcitivity, conducitvity and energy density [7]. The anther interesting research result reported by Zhang et al., [8] related with grephene oxide based other form of carbon compounds into nitrogen doped carbon composite (MnO@N doped/r-GO). After the incorporation of reduced graphene oxide into the manganese oxide latteice shows the improved structural stability by thermal treatment and also improved the supercapcitive performace [8]. Hence, in the present work new type of binary composite like Ni-Co doped MnO_2 coated with graphene oxide followed by Molbedenum sulphide additive on Nickel foam fabricated for the possible flexible device applications, which is shown schematically in Fig. 4. Structure, textural and electrochemical property of the binary nanocomposite have been studied in detail.

* Corresponding author: jrajabathar@ksu.edu.sa

2. Materials and method

All chemicals are used in the present work were of analytical grades. All other essential chemicals and graphene oxide powder are obtained from Sigma Aldrich and used without further purification.

2.2. Preparation of doping of Ni-Co-meso-MnO_2 by ultra-sonication method

The required quantity of Manganese sulphate (0.1 moles dissolved in 50 mL) solution is mixed with Triton X-100 (non-ionic surfactant) polymer solution (2mL dissolved in 240 mL of deionized water) and followed by the addition of Nickel (0.005 moles) and Cobalt (0.005 moles) salt is dissolved in 50 mL of deionized water and stirred for 10-15 min. Then, 0.1 M $NH_4S_2O_8$ was added dropwise to the above vigorously stirring (12 h) followed by calcined at 400 ^oC for 3 h to remove the surfactant. The above prepared Ni-Co-MnO_2 is added with R-GO(reduced graphene oxide) in ethanolic solution followed by ultra-sonicated for 10 minutes. In the second step is to addition of MoS_2required quantity (5-10 wt%) with above precipitated solid sample. The pristine meso-MnO_2/graphene/MoS_2 is prepared in the same way without addition of Ni-Co in the initial precursor solution and it's designated as MoSG-MnO_2.

2.3. Electro chemical analysis of as prepared MoS_2 and r-graphene oxide @meso-MnO_2 and and meso-Ni-Co-MnO_2

The as prepared modifed electrodes is consist of MoS_2 and graphene oxide on meso-Ni-Co-MnO_2 Ninanocomposite as major componet like above 90% was further mixed with few mL of nafion solution to form a paste and drying (at 80 ^oC) in an oven for two hours. The as prepared 5 mg of active material is pasted at the one end of Nickel foam followed by pressing the materials by 10 Mp pressure for 15 second. The electrolyte is a mixture of 1M H_2SO_4 and KI solution for better supporting electrolytic condition. Platinum wire electrode was used as counter electrode and silver chloride electrode as reference electrode (Fig. 4).

3. Results and discussion

Powder X-ray diffraction pattern of as prepared MoS_2 and graphene oxide modified Ni-Co-MnO_x are shown in Fig. 1 (a&b). The crystalline phase of binary nanocomposite (*hkl*) XRD pattern very much matched with the mesoporous Mn_2O_3 phase (JCPDS file number 24-0508). Some new peak appeared after deposition of MoS_2 on graphene oxide decorated Ni-Co-meso MnO_2, which is shown in Fig. 1.

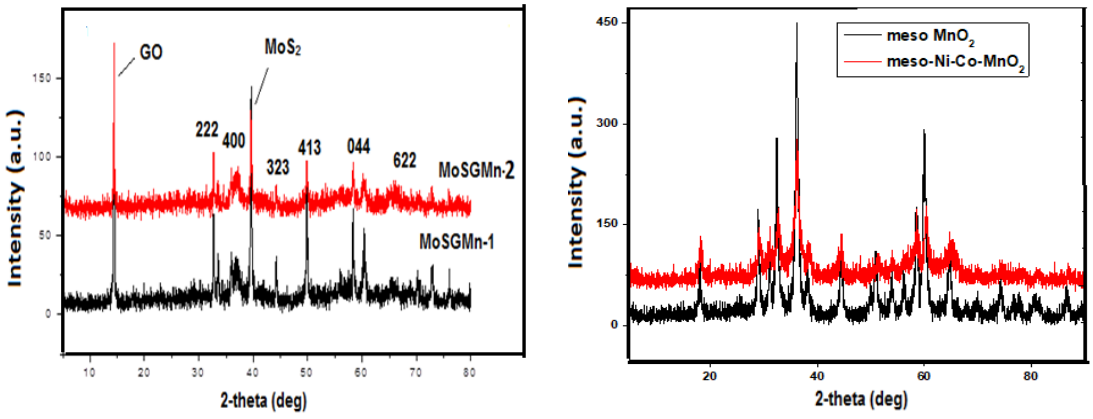

Fig. 1. Comparative XRD images (a) MoS_2-graphene @meso MnO_x (MoSGMn-1 &2) and (b) MoS_2-graphene@Ni-Co-mesoporous MnO_x.

The XRD peak at 2θ value of 15^o marked in Fig. 1a is due to presence of reudued graphene oxide in the as prepared nanocomposite, which is matched from reported resutls of reduced graphene oxide literature report [7-10]. The other peak at 2θ value 40^o is due to MoS_2, which is related with crystalline *hkl* value of (103) of bulk MoS_2 of the reported data [9]. Transmission electron micrographs of MoSG/Ni-Co@mesoporous MnO_2 and MoSG@MnO_2 (without Ni and Co addition) are shown in Fig. 2 (a-f). Fig. 2 a, b, c and d are exclusively shows in depth TEM images of newly prepared molybdenum sulphide/graphene modified Ni-Co-MnO_2 type binary nanocomposite prepared by our novel preparation methodology. Fig (2a &b) show the tiny fibers and nanorods foramtion with glassy morphology of graphene oxide in Fig. 2a. The lengthy fibers of MoS_2 are visible in Fig.2b. The Fig. 2c and 2d shows spherical particles and tiny tubuler shapes formation for Ni-Co doped manganese oxide composites and square and rectangle shapes in Fig. 2d are due to metallic particle formtion on glassy graphene oxide morphology. Fig. 2e and 2f shows TEM images of MoSGMnO_2-1 (75 mg MoS_2 added) and MoSGMnO_2-2 (50 mg), the dark metalic particles are caused by sticky formaiton of MnOx dispersion on RGO and MoS_2 nanoparticles. The MoS_2 particles forms the very tinny needle shape, due to decreased amount of MoS_2 incorporation in nanotube texture of manganese oxide. Fig. 2 e and f shows the needle like fiberous shape morphology, which is very visible at below 50 nm scale due to MoS_2 nanoparticle deposited on glassy morphology of reduced graphene oxide dispersion. Hence, the prepared Ni-Co doped MnO_2 is forms the nanotube morphology with spherical, rectangular and square type particles obtained in the range of 10 nm-20 nm.

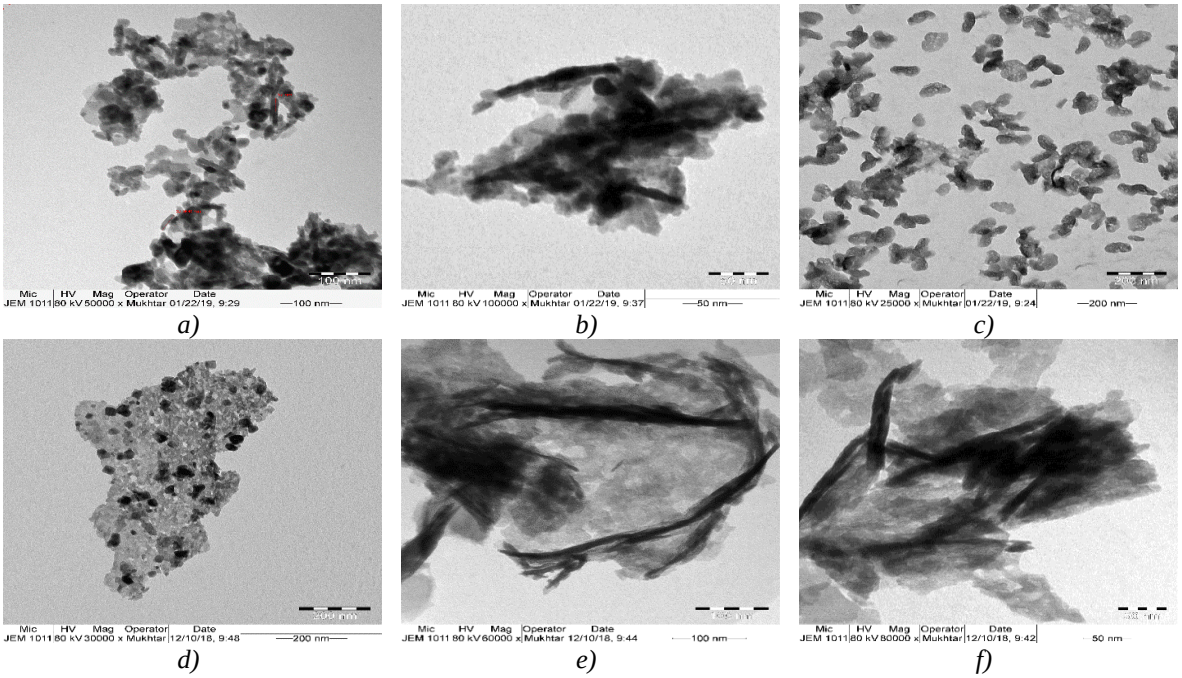

Fig. 2. TEM images of newly fabricated Ni-Co-meso MnO_2/Graphene/MoS_2 (a,b,c, d) compared with Pristine (without Ni and Co addition) sample (e and f).

The schematic image of as prepared nanocomposite fabrication on Nickel foam is shown in Fig. 4. The Cyclic voltammetry (CV) analysis results are provided in Fig. 3 (a-c) and Table 1 shows the physico- chemical property of as prepared binary nanocomposite such as surface area values and pore dimension values. Finally, we carry out the CV analysis over different amount of MoS_2 and RGO modified MnOx and Ni-Co-MnOx composites for exploits its potential electrochemical activity at different scan rates in acid electrolyte medium (1M sulphuric acid mixed with 1M KI solution). The potassium iodide is added to prevent the corrosion nature of the nickel foam electrode in acidic condtion. Fig. 3 (a-c) shows reactangle and leaf shape curves and there is no redox peaks formation. The specific capacitance values are given in Table 1 for all

analyzed nanocomposite modified nickel foam electrodes at fixed scan rate and the specific capacitance at different scan rate have also been studied. The much improved capacitance is obtained for MoS_2-graphene/Ni-$CoMnO_2$ compared to $MoSGMnO_2$-1 & 2. The as prepared modified electrode efficiency continusly decreases by decreasing in the incorporation weight percentage of MoS_2 in major manganese oxide compound. The leaf like structure of CV curves confirms that the modified electrode possess good electrical double-layer capacitance [10, 11]. The specific capacitance values are depending on the various factors such as the presence of micro and mesoporosity of electrode materials [12]. Secondly, 2D carbon network in graphene dispersion in manganese oxide enhances the electronic transition between electrode and electrolytic medium. The selected nanocomposite such as MoSGMn-1 and MoSGMn-2 is analyzed up to 1000 cycle number against specific capacitance retention stability and it provide satisfactory results. In addition, Fig. 3d shows the TGA results (thermogravimetric analysis) are further confirms that the enhanced thermal stability obtained for the as prepared $MoSGNiCoMnO_X$, major decomposition weight loss obtained after 650 ^oC. Hence, our method prepared novel designed Nickel foam based modified electrode exhibits a improved elecrochemical activity for binder free flexible device development.

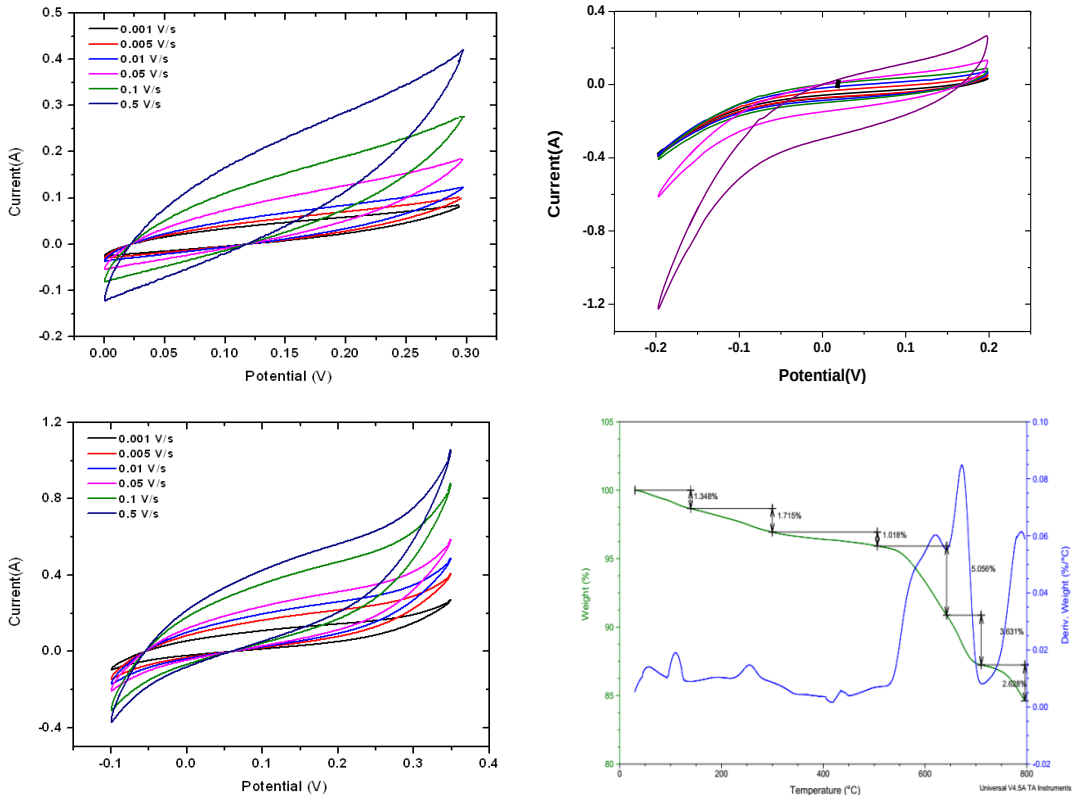

Fig. 3. (a-d) Cyclic voltammetry(CV) and Thermogravimetric analysis (TGA) for modified Ni-Co-meso-MnO_2 catalyst at different scan rates

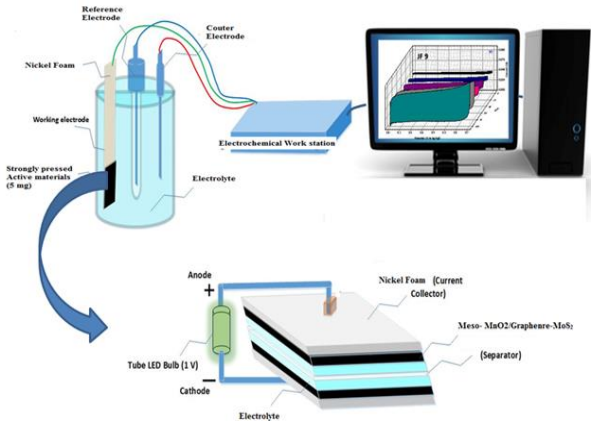

Fig. 4. (a) Schemtic of Nickel foam based hal cell working electrode setup (b) Our method based Nickel foam design setup for electrochemical analysis

Table 1. Physico chemcial property and electrochemical Specific capacitance (F/g) for MoS_2/RGO-NiCo-MnOx Nanocomposites

Scan rate (V/s)	**Specific Capacitance (F/g)**		
Sample Code	$MoSGMnO_2$-1	$MoSGMnO_2$-2	MoS_2/G-NiCo-MnO
Surfacearea (m^2/g)	110	114	102
Pore volume (cc/g)	0.04061	0.045061	0.05061
0.001 V/s	527	727	1190
0.005 V/s	134	93	550
0.01V/s	76	14.8	278
0.05 V/s	27	5.4	98
0.1V/s	17	4.1	65
0.5 V/s	5	1.63	45

4. Conclusions

The sandwitch type nanocomposite such as MoS_2/RGO deposited Ni-Co-mesoMnOx oxide with Mn_2O_3 like crystaline phase was prepared by precipitation and ultra-sonic deposition method. The binder free flexible electrode based on as prepared nanocomposite is fabricated with higher capacitance values with improved thermal stability. Ni-Co doped Manganese oxide is forms the smaller nanotube and spherical and square type particle less than 15 nm particle size are generated.

Acknowledgements

The authors are grateful to Deanship of Scientific research, King Saud University for financial support through Vice Deanship of Research Chairs.

References

[1] J. F. Da Costa-Serra, A. Chica, Int. J. Hydrogen Energy. **43**, 16859 (2018).
[2] J. Qiu, M. Guo, X. Wang, ACS Appl. Mater. Interfaces **3**, 2358 (2011).
[3] W. Lv, L. Li, Q. Meng, X. Zhang, J. Mater. Sci. **55**, 2492 (2020).
[4] M. Tamaddoni Saray, H. Hosseini, Electrochim. Acta. **222**, 505 (2016).
[5] C. Zhao, X. Lv, J. Li, T. Xie, Y. Qi, W. Chen, J. Electrochem. Soc. **164**, E505 (2017).
[6] M. Abecassis-Wolfovich, R. Jothiramalingam, M. V. Landau, M. Herskowitz, B. Viswanathan, T. K. Varadarajan, Appl. Catal. B Environ. **59**, 91 (2005).
[7] X. Cai, M. Peng, X. Yu, Y. Fu, D. Zou, J. Mater. Chem. C **2**, 1184 (2014).
[8] C. Zhang, Y. Zhang, Z. Miao, M. Ma, X. Du, J. Lin, B. Han, S. Takahashi, J.-I. Anzai, Q. Chen, Sensors Actuators, B Chem. **222**, 663 (2016).
[9] R. Jothi Ramalingam, Niketha Konikkara, Hamad Al-Lohedan, Dhaifallah M. Al-dhayan, L. John Kennedy, S. K. Khadheer Basha, Shaban R. M. Sayed, Int. J. Hydrog. Eng. **43**, 1712 (2018).
[10] R. Jothi Ramalingam, Niketha Konikkara, Hamad Al-Lohedan, Dhaifallah M. Al-dhayan, L. John Kennedy, S. K. Khadheer Basha, Shaban R. M. Sayed, International journal of hydrogen energy **43**, 17121 (2018).
[11] A. Mery, F. Ghamouss, C. Autret, D. Farhat, F. Tran-Van, J. Power Source **305**, 37 (2016).
[12] Q. Qu, P. Zhang, B. Wang, Y. Chen, S. Tian, Y. Wu, R. Holze, J. Phys. Chem. C **113**, 14020 (2009).