Vietnam Journal of Science and Technology ***57*** *(5) (2019) 585-593*

doi:10.15625/2525-2518/57/5/13313

PREPARATION AND CHARACTERIZATION OF GO/ZnO ELECTRODE FOR SUPERCAPACITORS

Hoang Tran Dung[1, *], Doan Thanh Tung[1, 2], Le Thi Thanh Tam[2], Trinh Quang Dung[1], Nguyen Thi Yen[1], Ngo Ba Thanh[1], Ngo Thanh Dung[2], Phan Ngoc Hong[2, 3], Le Trong Lu[1, 2, *]

[1]*Institute for Tropical Technology, VAST, 18 Hoang Quoc Viet, Cau Giay, Ha Noi*

[2]*Graduate University of Science and Technology, VAST, 18 Hoang Quoc Viet, Cau Giay, Ha Noi*

[3]*Center for High Technology Development, VAST, 18 Hoang Quoc Viet, Cau Giay, Ha Noi*

[*]Email: *ltlu@itt.vast.vn; htdung@itt.vast.vn*

Received: 21 November 2018; Accepted for publication: 6 September 2019

Abstract. The combination of metal oxide nanoparticles and advanced carbon-based materials such as graphene, carbon nanotubes (CNTs), graphene oxide (GO) etc. has received much attention due to their potential applications in power storage devices as supercapacitors. In this paper, zinc oxide (ZnO) nanoparticles were prepared by thermal decomposition of Zn (II) acetylacetonate in octadecene using oleic acid/oleylamine as surfactants and octadecanol as accelerating agent. A mixture of ZnO nanoparticles and GO, surfactants, binders are dispersed in aqueous solvent. This suspension was then used as the ink for the modified 3D printer to coat on the graphite substrate to form electrodes. The GO/ZnO film has a specific capacitance of 119.9 F/g at a scan rate of 5 mV/s of CV test. The specific discharge capacitance was 153.9 F/g and retained 94.5 % after 3000 cycles of galvanostatic charge-discharge (GCD) measurement with a current density of 15 mA/cm^2.

Keywords: electrode, nanomaterials, supercapacitors, 3D printer.

Classification numbers: 2.4.4, 2.8.2.

1. INTRODUCTION

Recently, supercapacitors (SCs) have become important in the field of energy storage and conversion due to its superior features, including super-fast charging/discharging time, long life and high power density [1-4]. These characteristics make SCs a potential alternative or complementary component to traditional batteries in applications that require fast charging/discharging and high currents in short periods of time. However, the SCs have the disadvantage of lower energy density than traditional batteries. In order to improve the energy density of SCs, most of the current studies are focused on the development of new electrode materials with higher performance. Thus far, carbon-based materials (activated carbon, CNTs and graphene) which have large specific surface area, chemical stability and high conductivity

have been widely used as electrode materials for electric double layer capacitors [5-10]. On the other hand, ferrite, hydroxide or oxide materials (Co, Mn, Ni, Ru, Zn…) have been studied to use as SCs electrode materials due to their high charge capacitance and rapid surface redox reactions [11-14]. In addition, the study on hybrid materials of carbon and metal oxides as SCs electrode materials has recently attracted increasing attentions [15-18]. Graphene oxide (GO) has recently emerged as a new carbon-based material made of oxidizing graphite crystals capable of providing high quantity at low cost. The GO-ZnO nanoparticle electrode material exhibits the potential for supercapacitor applications [19]. In our previous works, we have developed a modified 3D printer and reported the preparation of CNTs/$CoFe_2O_4$ nanoparticles hybrid supercapacitor electrodes by printing process [20, 21]. However, the specific capacitance of the prepared electrode was still low and the relatively expensive and not environmentally friendly $CoFe_2O_4$ nanomaterial was used in the ink formula. Besides, $CoFe_2O_4$, CoFe and Fe_3O_4 nanoparticles have been successfully synthesized by thermal decomposition of organometallic precursors in organic solvent [22-25].

In this paper, we present the results on the preparation of GO/ZnO nanoparticles suspension as ink for the modified 3D printer. The SCs electrodes were fabricated by printing method this is an efficient and eco-friendly procedure. The materials and SCs electrodes are investigated by various techniques of scanning electron microscopy (SEM), Energy Dispersive X-Ray Analysis (EDX), transmission electron microscopy (TEM), ultraviolet–visible spectrophotometry (UV-Vis), Raman spectroscopy, cyclic voltammetry (CV), and galvanostatic charge-discharge (GCD) measurements.

2. MATERIALS AND EXPERIMENTAL

2.1. Materials

Zinc (II) acetylacetonate 99.9 % ($Zn(acac)_2$), oleylamine (OLA) 70 %, oleic acid (OA) technical grade, octadecanol (OCD-ol), octadecene, polyvinyl alcohol (PVA), dodecyl sulfate (SDS), hexane, ethanol, potassium hydroxide (KOH) are ordered from Sigma-Aldrich (Singapore). Graphene oxide (GO) were synthesized using modified Hummer's method by Center for Advanced Material Development. All the chemicals were used as received without further purification.

2.2. Experimental

2.2.1. Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized by thermal decomposition of organometallic precursors of Zn ($Zn(acac)_2$) in octadecene using OA/OLA as surfactant and OCD-ol as accelerating agent. In a typical synthesis, $Zn(acac)_2$ (4.48 g, 17 mmol), OCD-ol (7.2 g, 26.6 mmol) were added into a 100 mL three necked round bottom flask in the presence of a mixture of 14 mL OA and 7.2 mL OLA. The octadecene solvent was used with a volume of 40 mL. The mixture was magnetic stirred and degassed for 30 min at room temperature. The reaction mixture was heated to 100 °C and kept at this temperature for 30 minutes in order to remove water. The temperature was then raised to 200 °C, and sustained for another 30 min before being increased to 295 °C (heating rate of 7-8 °C/min). The whole process is conducted under continuous nitrogen flow. Before characterizations, the as-synthesized nanoparticles were purified from free excess ligands. Typically, 5 mL of a solution of nanoparticles was mixed with

10 mL of ethanol. Nanoparticles were collected by centrifugation at 8,000-12,000 rpm for 8 min until nanoparticles were precipitated and the supernatant was discarded. The precipitated nanoparticles were then re-dispersed in 0.5 mL n-hexane. This precipitation/re-dispersion procedure was carried out more 2 times. Finally, the nanoparticles were dispersed in 0.5 mL n-hexane.

2.2.2. Printing electrode

The GO/ZnO electrode was fabricated using the printing process (Fig. 1) by a modified 3D printer with mixed materials as ink [20]. The weight ratios of ZnO nanoparticles over GO were kept at 0 %, 20 % and 40 %. Typically, 76 mg powder mixture of GO and ZnO nanoparticles with (m_{ZnO}/m_{GO} = 0 %, 20 % or 40 %), 2 mg of PVA and 2 mg of SDS were mixed in 2 mL of distilled water at 60 °C for 30 min by magnetic stirrer then sonication was used to form a good dispersion. The suspension was printed on graphite paper to form electrodes. The printed electrodes were baked in an oven at 200 °C for 6 hrs and then stored at room condition. The samples of electrodes made from mixture of GO and ZnO with weight ratios of 0 %, 20 % and 40 % are labeled GZ-0, GZ-20 and GZ-40, respectively.

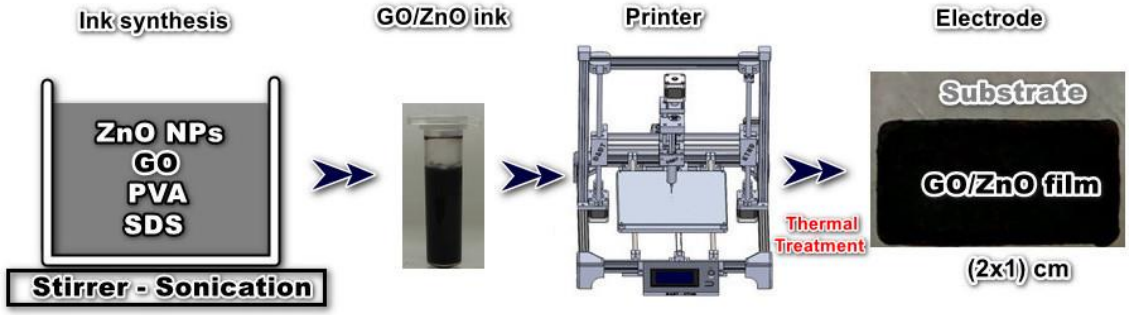

Figure 1. The process of printing electrode.

2.3. Characterizations

The transmission electron microscopy (TEM, Jeol JEM-1010 microscope) was used to investigate the morphology of synthesized ZnO nanoparticles. The optical absorption of the ZnO nanoparticles was measured using a UV-Vis Spectrometers (CINTRA 40, GBC) in the wavelength range of 200–900 nm at room temperature. The morphology and the elemental composition of printed GO/ZnO film were observed by scanning electron microscopy (SEM-EDX, Hitachi S-4800 microscope). Raman spectra were recorded using a XploRA Plus Raman spectrophotometer (with 532 nm laser).

Electrochemical properties of the printed GO/ZnO electrodes were characterized by a potentiostat/galvanostat (Bio-Logic, VSP-300) using CV and GCD method with a standard three – electrode cell. The electrolyte was composed of 6 M KOH in distilled water. A platinum foil was used as counter electrode. Saturated calomel electrode (SCE) is a reference electrode and working electrode was GO/ZnO film printed on graphite paper substrate.

3. RESULTS AND DISCUSSION

3.1. Material characterization

The UV-visible absorption spectrum of the ZnO nanoparticles is shown in Fig. 2a. It can be seen that the sample has an absorption edge at wavelength of 378 nm. The optical band gap of the film is determined by applying the Tauc model [26]

$$\alpha h\nu = A(h\nu - E_g)^{\frac{1}{2}} \quad (1)$$

where $h\nu$ is the photon energy, A is the constant, and E_g is the optical band gap.

By plotting $(\alpha h\nu)^2$ versus $h\nu$ (Fig. 2b) and extrapolating the linear portion of the absorption edge to find the intercept with energy axis, the calculated optical band gap of synthesized ZnO nanoparticles was 3.32 eV. The results are similar to the optical characteristics of reported ZnO nanoparticles.

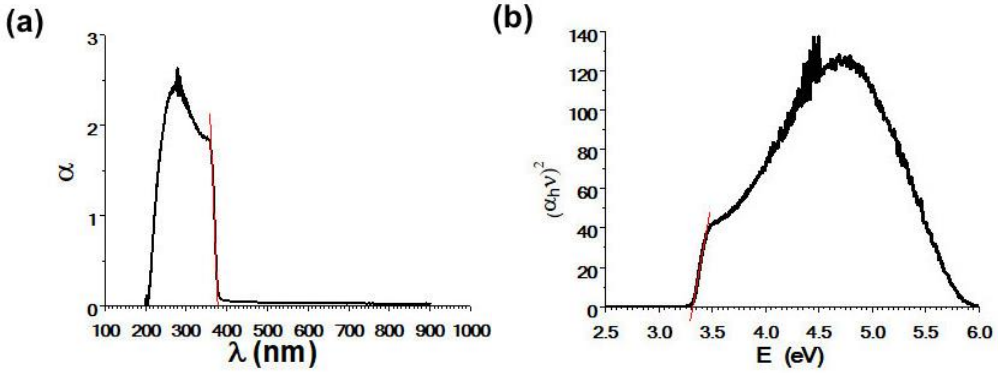

Figure 2. UV-visible absorption spectrum of the ZnO nanoparticles (a), and the $(\alpha h\nu)^2$ versus $h\nu$ curves for the optical band gap determination.

Figure 3a shows TEM image of ZnO nanoparticles. It can be realized that ZnO nanoparticles are in mainly spherical and pyramidal shape with an average size of ca. 20 nm. The SEM images clearly show GO's leaf structure (Figure 3b, c, d). ZnO nanoparticles are distributed on the GO surface, form a rather large cluster of particles. The GZ-40 sample has a significantly higher number of seeds than the GZ-20 sample.

In addition, the EDX measurements was performed to analyze the composition of the printed films. Fig. 4 indicates the EDX spectrum of GZ-40 sample. It is seen that the obtained film contains carbon, zinc and oxygen which proves the existence of the GO/ZnO film on the substrate. The presence of sulfur element in the EDX spectrum stems from the SDS surfactant used in the sample. From the SEM images, it is observed that some ZnO nanoparticles were aggregated on the GO sheets. The aggregation of ZnO nanoparticles on GO sheets in the obtained film can affect the electrochemical properties of the electrode.

The Raman analysis was performed with the two printed electrode samples GZ-0 (only GO) before and after heat treatment at 200 ^oC. In Fig. 5a, GO before thermal treatment has the D peak at 1342.55 cm^{-1}, the G peak at 1577.69 cm^{-1} and $I_D/I_G \approx 1.12$. For GO was thermal treated at 200 ^oC, the D peak and G peak of it located at 1309.76 cm^{-1} and at 1600.68 cm^{-1} respectively with $I_D/I_G \approx 1.43$. The intensity of the D band is related to the size of the in-plane sp^2 domains. The increase of the D peak intensity indicates forming more sp^2 domains. So, the GO had been reduced to reduced GO (rGO) and electrical conductivity of it was increased [27, 28].

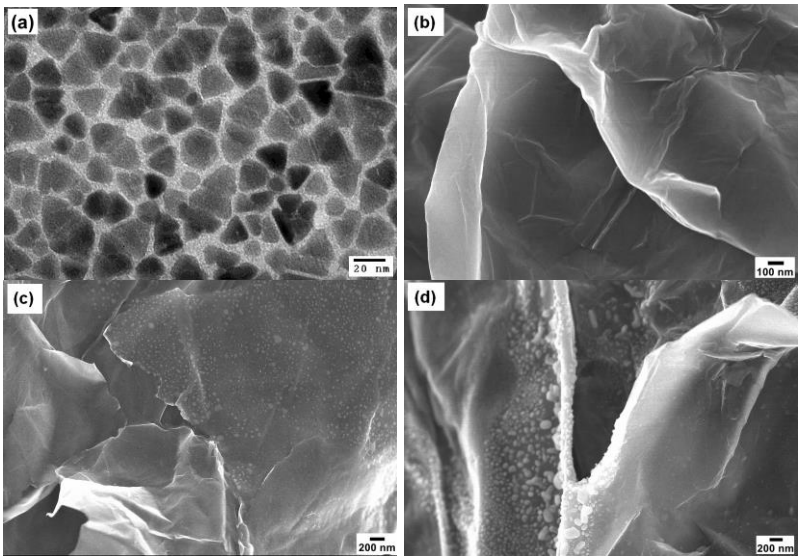

Figure 3. TEM image of ZnO nanoparticles (a), SEM images of GO/ZnO films: GZ-0 (b), GZ-20 (c) and GZ-40 (d).

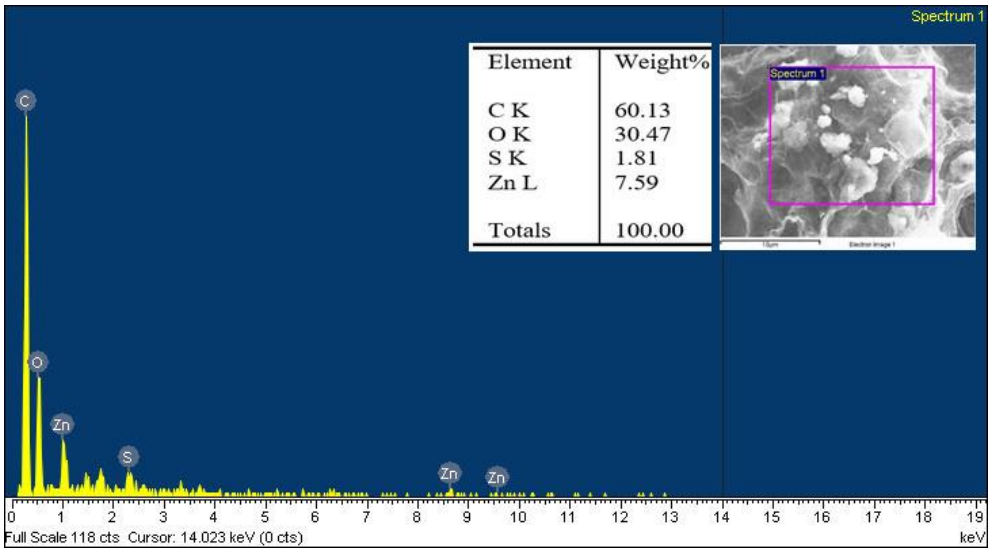

Figure 4. EDX spectrum of GZ-40.

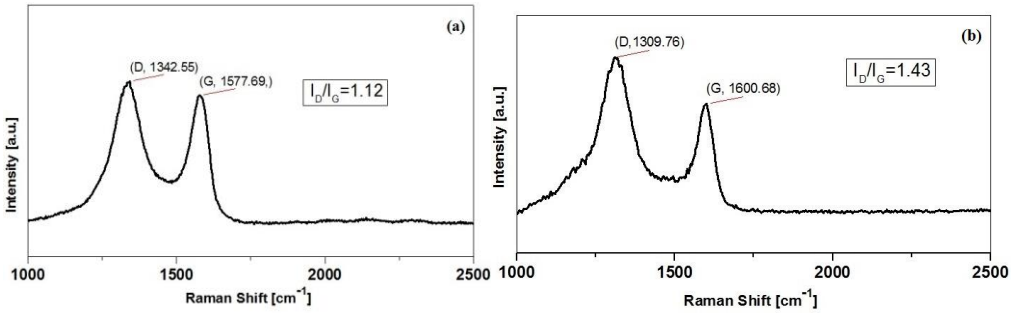

Figure 5. Raman spectrum of GZ-0 (a) without thermal treatment, (b) with 200 ^{o}C thermal treatment.

3.2. Electrochemical measurements

Figure 6a-c show the CV curves of GZ-0, GZ-20, and GZ-40 at different scan rates of 5, 10, 20, 50, and 100 mV/s.

The specific capacitance (C_s) of testing electrodes is calculated from CV curves using the formula:

$$C_s = \frac{\int_{V_a}^{V_b} i(V)dV}{2 \times v \times m \times |V_b - V_a|} = \frac{S}{2 \times v \times m \times \Delta V} \quad (2)$$

where S is the area of the CV curve, v is the scan rate, m is the mass of the active material in working electrode (if vertical axis of cv curve is the current density, m is ignored because the current density includes m), and ΔV is the working potential window.

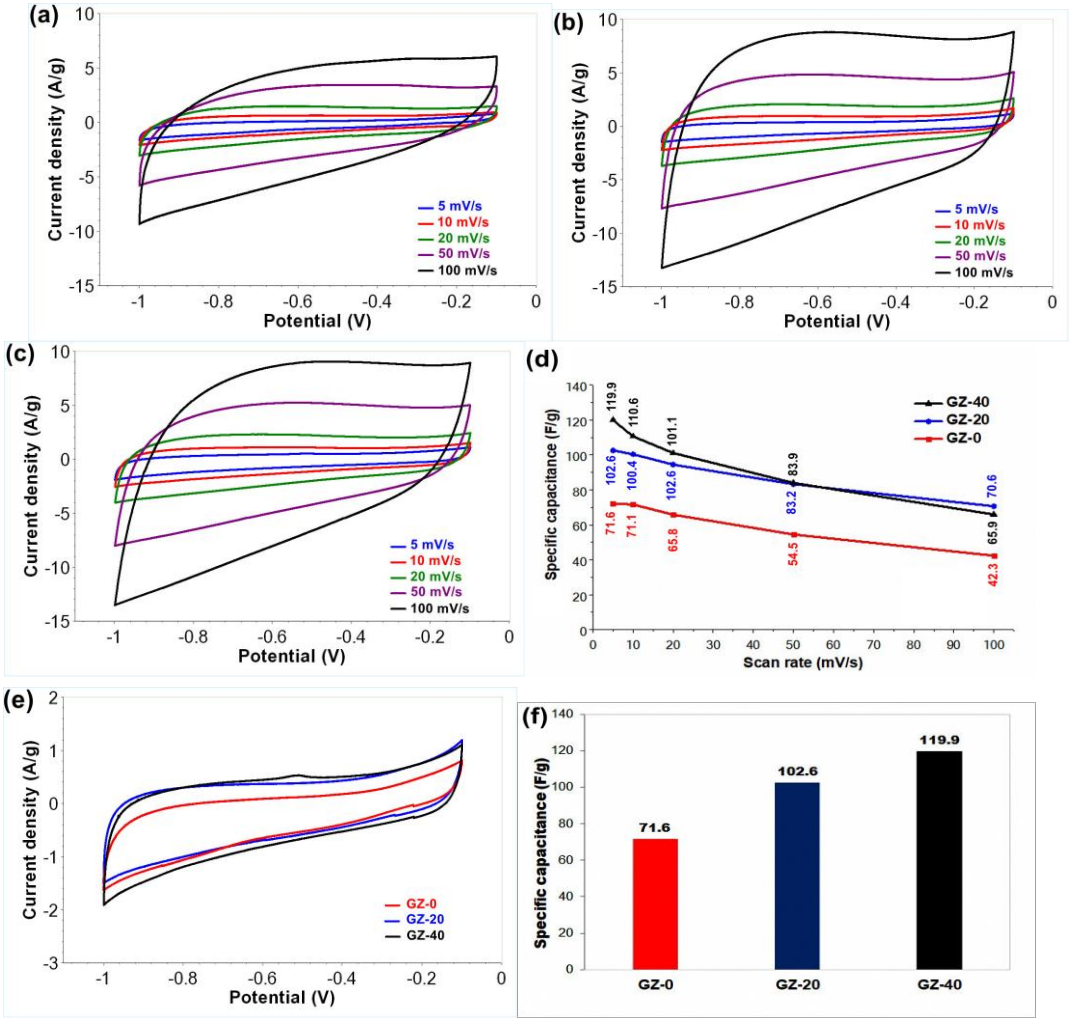

Figure 6. CV curves of GZ-0 (a), GZ-20 (b), GZ-40 (c); Specific capacitance of GZ-0, GZ-20, and GZ-40 at different scan rates (d); Comparison of CV curves at 5 mV/s scan rate (e), and the calculated specific capacitance of the samples(f).

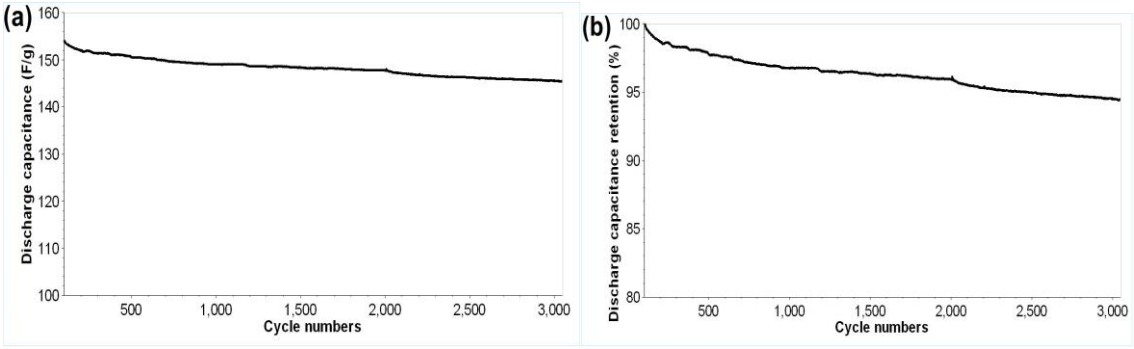

Figure 7. GCD curve of GZ-40 (a) and discharge capacitance retention vs. cycle number (b).

In comparison, the CV curves of three samples at a scan rate of 5 mV/s were shown in Fig. 6e and the calculated specific capacitance of GZ-0, GZ-20, and GZ-40 at a scan rate of 5 mV/s in the potential range from -1 V to -0.1 V are 71.6 F/g, 102.6 F/g, and 119.9 F/g, respectively (Fig. 6f). It is noted that the capacitance of the electrode is increased with the addition of ZnO nanoparticles. The porosity of the GO film is possibly changed after adding nanoparticles due to the formation of aggregated nanoparticles on GO sheets made them split apart instead of being stacked together as GO films without nanoparticles. Thus, the specific capacitance of the electrodes was enhanced because of the increasing of surface area of the electrode. In addition, the specific capacitance of GO/ZnO is improved because of the storing charge based on pseudo-capacitance mechanism of ZnO nanoparticles. The possible faradic process can be explained as follows [29]:

$$ZnO + OH^- \leftrightarrow ZnOOH + e^- \quad (3)$$

The GCD measurement with a charge-discharge current density of 15 mA/cm^2 was conducted with GZ-40 sample to evaluate the stability of the working electrode. The GCD curve of GZ-40 is shown in Fig. 7a. After 3000 cycles, the discharge capacitance is maintained at 94.5 % initial value (Fig. 7b) suggests that the prepared electrode is highly electrochemical stable.

4. CONCLUSIONS

In conclusion, ZnO nanoparticles were successfully synthesized by thermal decomposition of Zn (II) acetylacetonate in octadecene using oleic acid/oleylamine as surfactants and octadecanol as accelerating agent. The mixture of ZnO nanoparticles and GO, surfactants, binders dispersed in aqueous solvent was used as ink for the modified 3D printer to deposit on the graphite substrate to form electrodes. After heat treatment, the printed GO/ZnO electrode has a specific capacitance of 119.9 F/g at a scan rate of 5 mV/s of CV test. In GCD test with a current density of 15 mA/cm^2, the specific discharge capacitance of GO/ZnO electrode was 153.9 F/g and retained 94.5 % after 3000 cycles. This indicates that the printed GO/ZnO electrode has potential for application to supercapacitors.

Acknowledgements. This work was financial supported by Institute for Tropical Technology (2018 annual project), Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.02-2018.66 and Vietnam Academy of Science and Technology (VAST01.08/19-20 project).

REFERENCES

1. Iro Z. S., Subramani C., Das S. S. - A brief review on electrode materials for supercapacitor, Int. J. Electrochem. Sci. **11** (2016) 10628-10643.
2. Halper M. S., Ellenbogen J. C - Supercapacitors: A brief overview, The MITRE Corporation, McLean, Virginia, Mar 2006.
3. Wang G. P., Zhang L., Zhang J. J. - A review of electrode materials for electrochemical supercapacitors, Chem. Soc. Rev. **41** (2012) 797-828.
4. Simon P., Gogotsi Y. - Materials for electrochemical capacitors, Nat. Mater. **7** (2008) 845-854.
5. Hsieh C. T., Chen Y. C., Chen Y. F., Huq M. M., Chen P. Y., Jang B. S. - Microwave synthesis of titania-coated carbon nanotube composites for electrochemical capacitors, J. Power Sources **269** (2014) 526-533.
6. Liu C. G., Yu Z. N., Neff D., Zhamu A., Jang B. Z. - Graphene-based supercapacitor with an ultrahigh energy density, Nano Lett. **10** (2010) 4863-4868.
7. Chen J., Xia N., Zhou T., Tan S., Jiang F., Yuan D. - Mesoporous carbon spheres: Synthesis, characterization and supercapacitance, Int. J. Electrochem. Sci. **4** (2009) 1063-1073.
8. Zhu Y., Elim H. I., Foo Y. L., Yu T., Liu Y., Ji W., Lee J.Y., Shen Z., Wee A. T. S., Thong J.T.L. -Multiwalled carbon nanotubes beaded with ZnO nanoparticles for ultrafast nonlinear optical switching, Adv. Mater. **18** (2006) 587-592.
9. Du C., Yeh J., and Pan N. - High power density supercapacitors using locally aligned carbon nanotube electrodes, Nanotechnology **16** (2005) 350-353.
10. Van Man Tran, Dinh Tan Phat Pham, Huu Tru Nguyen, Van Hoang Nguyen, My Loan Phung Le - Tra Bac activated carbon used as electrode material in aqueous supercapacitor, Vietnam Journal of Science and Technology **55** (1B) (2017) 257–265.
11. Yang P. H., Ding Y., Lin Z. Y., Chen Z. W., Li Y. Z., Qiang P. F., Ebrahimi M., Mai W. J., Wong C. P., and Wang Z. L. - Low-cost high-performance solid-state asymmetric supercapacitors based on MnO_2 nanowires and Fe_2O_3 nanotubes, Nano Letter **14** (2014) 731-736.
12. Yu G. H., Xie X., Pan L. J., Bao Z. N., Cui Y. - Hybrid nanostructured materials for high-performance electrochemical capacitors, Nano Energy **2** (2013) 213-234.
13. Ates M. and Fernandez C. - Ruthenium oxide–carbon-based nanofiller-reinforced conducting polymer nanocomposites and their supercapacitor applications, Polym. Bull. **76** (5) (2019) 2601–2619.
14. Purushothaman K. K., Suba Priya V., Nagamuthu S., Vijayakumar S., Muralidharan G. - Synthesising of ZnO nanopetals for supercapacitor applications, Micro & Nano Letters **6** (8) (2011) 668-670.
15. Wang Y. Y., Xiao X., Xue H.G., and Pang H. - Zinc oxide based composite materials for advanced supercapacitors, ChemistrySelect **3** (2018) 550-565.
16. Aravinda L., Nagaraja K., Nagaraja H., Bhat K. U., and Bhat B. R. - ZnO/carbon nanotube nanocomposite for high energy density supercapacitors, Electrochimica Acta **95** (2013) 119-124.
17. Lee S. W., Kim J., Chen S., Hammond P. T., and Shao-Horn Y. - Carbon nanotube/manganese oxide ultrathin film electrodes for electrochemical capacitors, ACS Nano **4** (2010) 3889-3896.

18. Lin P., She Q., Hong B., Liu X., Shi Y., Shi Z., Zheng M., and Dong Q. - The nickel oxide/CNT composites with high capacitance for supercapacitor, J. Electrochem. Soc. **157** (7) (2010) A818-A823.
19. Rajeswari V., Jayavel R., Dhanemozhi A. C. - Synthesis and characterization of graphene-zinc oxide nanocomposite electrode material for supercapacitor applications, Materials Today: Proceedings **4** (2017) 645-652.
20. Hoang Tran Dung, Ngo Thanh Dung, Trinh Quang Dung, Doan Thanh Tung, Nguyen Thi Yen, Le Thi Thanh Tam, Tran Viet Thu, Phan Ngoc Hong, Le Trong Lu - Fabrication and characterization of supercapacitor electrode by 3D printing, Vietnam Journal of Science and Technology **56** (5) (2018) 574-581.
21. Le T. T. Tam, Nguyen V. Hung, Doan T. Tung, Ngo T. Dung, Hoang T. Dung, Nguyen T. Dung, Phan N. Minh, Phan N. Hong, Le T. Lu - Synthesis and electrochemical properties of porous CNTs-ferrite hybrid nanostructures for supercapacitor, Vietnam Journal of Science and Technology **57** (1) (2019) 58-66.
22. Le T. Lu, Ngo T. Dung, Le D. Tung, Cao T. Thanh, Ong K. Quy, Nguyen V. Chuc, Shinya Maenosonoe and Nguyen T. K. Thanh - Synthesis of magnetic cobalt ferrite nanoparticles with controlled morphology, monodispersity and composition: the influence of solvent, surfactant, reductant and synthetic conditions, Nanoscale **7** (46) (2015) 9596–19610.
23. Pham H. Nam, Le T. Lu, Pham H. Linh, Do H. Manh, Le T. T. Tam, Nguyen X. Phuc, Pham T. Phong, In-Ja Lee - Polymer-coated cobalt ferrite nanoparticles: Synthesis, characterization, and toxicity for hyperthermia applications, New J. Chem. **42** (17) (2018) 14530-14541.
24. Thanh Dung Ngo, Thi My Hanh Le, The Huu Nguyen, Thien Vuong Nguyen, Tuan Anh Nguyen, Trong Lu Le, Thi Thai Nguyen, Thi Thanh Van Tran, Thi Bich Thao Le and Ngoc Hai Doan - Antibacterial nanocomposites based on Fe_3O_4–Ag hybrid nanoparticles and natural rubber-polyethylene blends, Int. J. Poly. Sci. **2016** (2016), article ID 7478161, 9 pages.
25. Ngo T. Dung, Nguyen Viet Long, Le T. T. Tam, Pham H. Nam, Le D. Tung, Nguyen X. Phuc, Le T. Lu and Nguyen Thi Kim Thanh - High magnetisation, monodisperse and water-dispersible CoFe@Pt core/shell nanoparticles, Nanoscale **9** (26) (2017), 8893–9248.
26. Li X. Y., Li H. J., Wang Z. J., Xia H., Xiong Z. Y., Wang J. X., Yang B. C. – Effect of substrate temperature on the structural and optical properties of ZnO and Al-doped ZnO thin films prepared by dc magnetron sputtering, Optics Communications **282** (2009) 247-252.
27. Hayes W. I., Joseph P., Mughal M. Z., Papakonstantinou P. – Production of reduced graphene oxide via hydrothermal reduction in an aqueous sulphuric acid suspension and its electrochemical behaviour, J. Solid State Electrochem. **19** (2) (2015) 361-380.
28. Kaushal A., Dhawan S. K., and Singh V. - Determination of crystallite size, number of graphene layers and defect density of graphene oxide (GO) and reduced graphene oxide (RGO), AIP Conference Proceedings **2115** (2019) 030106.
29. Saranya M., Ramachandran R., Wang F. - Graphene-zinc oxide (G-ZnO) nanocomposite for electrochemical supercapacitor applications, Journal of Science: Advanced Materials and Devices **1** (4) (2016) 454-460.