Synthesis and Characterization of Sol-Gel Derived $Bivo_4$ Nanoparticles for Electrochemical Applications

R. Packiaraj, K. S. Venkatesh, P. Devendran, S. Asath Bahadur, N. Nallamuthu

Abstract: ***$BiVO_4$ nanoparticles (NPs) were prepared sol-gel technique for the potential electrode of supercapacitor applications. The crystal structure, elemental composition, and surface morphology of the synthesized sample were characterized by powder X-ray diffraction (PXRD), scanning electron microscopy and elemental analysis (EDS) spectrum, respectively. The diffraction peaks were well indexed with monoclinic structure. The morphology of the synthesized sample exhibited that small flattened rice shaped structure with the average particle size of ~50 nm. The room temperature capacitive behaviour of $BiVO_4$ NPs electrode was recorded by cyclic voltammetry (CV) in 2 M of KOH electrolyte. The enhance specific capacitance (C_{SP}= 139 F g^{-1}) was observed at the scan rate of ~10 mVs^{-1}. The results show that the as synthesized $BiVO_4$ NPs is a potential candidate for electrochemical supercapacitor application.***

Keywords: PXRD, Monoclinic, Cyclic Voltammetry, Specific capacitance, Supercapacitor.

I. INTRODUCTION

Among the exhaustion of remnant energy, global warming and pollution, renewable energy capital have involved an enormous amount of concentration [1]. The insist for electrochemical energy storage devices have enlarged in the past few years. With the energy storage devices, supercapacitors [SCs] are considered one of the majority promising device due to their specific power being as high as conservative capacitors and a specific energy close to that of batteries, as well as their other advantages : eco-friendly and comparatively low cost [2]. Among the numerous supercapacitor based electrodes, pseudocapacitive based transition-metal oxides or inorganic compounds showed large energy density due to faradic redox charge storage mechanism, which has higher energy density compared to the electrochemical double-Layer capacitive carbon materials [3, 4]. In pseudocapacitors, the electrochemical charge storage is done by Faradic redox reactions. The pseudocapacitors based electrodes were fabricated by means of conducting polymers, metal oxides and hydroxides. Particularly some materials such as polyaniline, $NiMoO_4$, NiO, Co_3O_4 and MnO_2 were used as pseudocapacitors electrodes [5]. In this present study demonstrate the synthesized $BiVO_4$ modified working electrode used as a pseudocapacitor electrode material for supercapacitor application. Based on the previous reports, $BiVO_4$ used as efficacy photocatalyst, phosphor hosts, sensors and an electrode for electrochemical devices, etc. [6]. For the past few years, a small number of efforts have been made to use $BiVO_4$ as a pseudocapacitive material for high – performance supercapacitors because of its better electrical conductivity and high specific capacitance [7]. As we known, the synergistic effect of bismuth species and Vanadium species plays important roles in the high electrochemical performance of Bismuth vanadium binary oxides. Therefore, the bismuth vanadium binary metal oxides are expected to deliver higher supercapacitive performance than both bismuth oxide and vanadium oxides [8].

Herein, we report the synthesis of $BiVO_4$ NPs by a simplistic and eco – friendly sol-gel technique. The $BiVO_4$ sample loaded modified working electrode improved the electrochemical performance. The $BiVO_4$ modified electrode revealed the highest specific capacitance 139 Fg^{-1} at 10 mVs^{-1}.

II. EXPERIMENTAL

A. *Sample preparation*

All the starting precursors were purchased with AR grade and used for preparation without any addition further purification process. The BiVO4 NPs were synthesized by sol-gel method using Bi(NO3)3·5H2O (bismuth nitrate pentahydrate), NH4VO3 (ammonium metavanadate), HNO3 (Nitric acid), NH4OH (ammonium hydroxide) and CH3COOH (acetic acid) as the starting materials. In the typical synthesis, the stoichiometric amount of the starting precursors such as Bi $(NO_3)_3{\cdot}5H_2O$ and NH_4VO_3 chemicals were dissolved in 50 ml of double distilled (DD) water, separately. The above two solutions were mixed together. Additionally, 100 ml of ethanol was dropped wise added into the solution and hence the stirrer heat was increased at 70 ^oC. The yellow sol was formed.

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* Correspondence Author
N. Nallamuthu*, Department of Physics, Kalasalingam Academy of Research and Education, Krishnankoil – 626126. Tamil Nadu, India. Email: n.nallamuthu@klu.ac.in
R. Packiaraj, Department of Physics, Kalasalingam Academy of Research and Education, Krishnankoil – 626126.Tamil Nadu, India. Email: newtonrajphy@gmail.com
K.S. Venkatesh, Department of Physics, Syed Ammal Arts and Science College, Ramanathapuram, Tamil Nadu 623513, India, venkatesh10685@gmail.com
P. Devendran, Department of Physics, Kalasalingam Academy of Research and Education, Krishnankoil – 626126.Tamil Nadu, India. Email: pdevavenmani@gmail.com
S. Asath Bahadur, Department of Physics, Kalasalingam Academy of Research and Education, Krishnankoil – 626126.Tamil Nadu, India. Email: s_a_bahadur@yahoo.co.in

Further 1M of acetic acid (CH_3COOH) to make a 50 ml stock solution, the solution was added drop wise the solution maintained at 100 ^oC for a few hrs. The gel was collected and calcined at 600 ^oC in the furnace. The pure monoclinic $BiVO_4$ sample was formed.

III. RESULTS AND DISCUSSION

A. PXRD

The crystal structural and phase identification analysis of sol-gel derived $BiVO_4$ sample were characterized by powder X-ray Diffraction (PXRD) technique. The XRD pattern of $BiVO_4$ material is as shown in Fig. 1. The sharp powder X ray diffraction peaks showed that the sample has the high crystalline nature. The diffraction peaks are completely matched and good aggreement with the reference pattern of monoclinic-$BiVO_4$ (JCPDS card no- 75-1866) and with the space group I2/a [9]. No more other peaks are observed in these patterns. The crystalline size was measured by using Scherer's equation, the average size of the particle is ~26 nm.

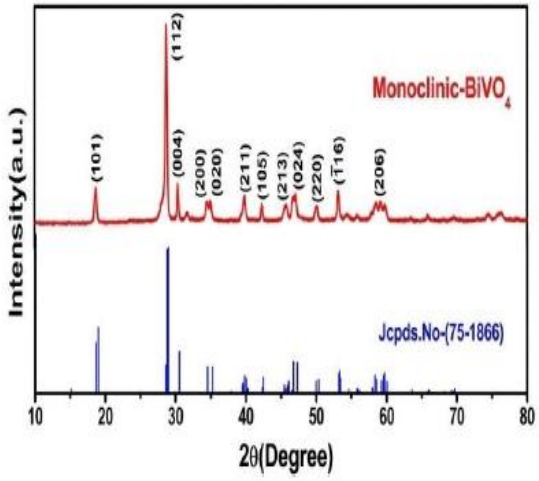

Fig. 1.XRD pattern of Monoclinic $BiVO_4$

B. SEM and EDX Analysis

The surface micrographs and present elements of the $BiVO_4$ sample was analyzed using SEM and EDX analysis. The SEM images of $BiVO_4$ were recorded with different magnifications and the SEM images are displayed in Fig. 2(a,b). The particles clearly show that the flattened rice shaped morphology for pure $BiVO_4$ (Fig. 2 (a & b)). From the SEM analysis the average size of the particle is measured. The mean size of the particle is ~50 nm. Fig.2. (c) EDX spectrum shows the purity of the sample. This is at last affirmed the presence of the elements such as Bi, V and O and no other extra impurity peaks detected which completely
favors the preparation $BiVO_4$ material through sol-gel technique.

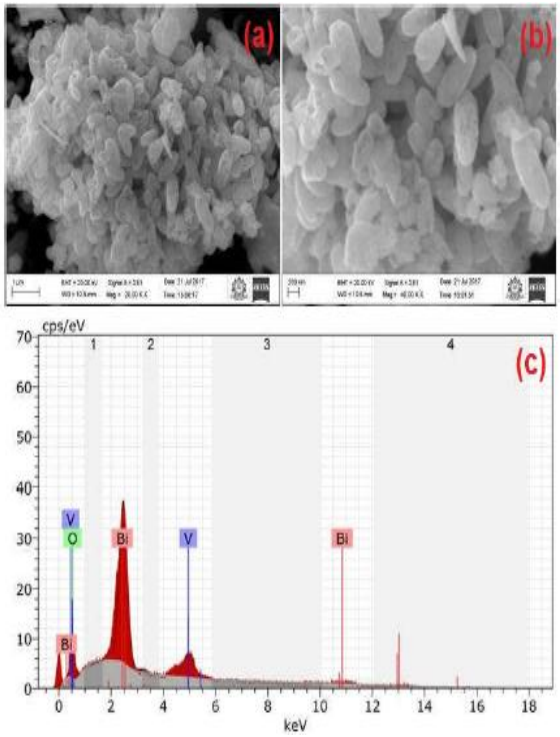

Fig. 2.SEM and EDX pattern of Monoclinic $BiVO_4$

C. *Cyclic Voltammetry Analysis*

The Cyclic Voltammetry (CV) is major tool to investigate the electrochemical behaviour of the sample modified electrode. This is confirming the either EDLC or Pseudocapacitance nature. The prepared sample was coated on nickel foam which act as a working electrode, reference electrode is Ag/Agcl and platinum wire is act as a counter electrode. The entire reaction was tested by 2M KOH solution. The Cyclic Voltammetry graph is shown in fig. 3a. From the CV graph divulged the pseduocapacitance nature of the $BiVO_4$ sample. The faradaic redox reactions were take place on the surface of the electrode material.

$$BiVO_4 + xK_+ + xe \leftrightarrow Kx\ BiVO_4 \quad (1)$$

Where, x represents the mole concentration of K^+ ions. There can be seen that there are one anodic and one cathodic peak in the CV graph as shown in Fig. 3a. The appearance of the anodic peak at -0.7 V occurrence of Bi^{3+} to Bi^0. The peak current versus the square root of the scan rate of the $BiVO_4$ NPs is shown in Fig. 3b. This indicates a linear relationship between peak current and square root scan rate, it denotes the electrode reaction is diffusion-controlled. The presence of cathodic peak at -0.2 V attributes the reduction reaction of Bi metal to Bi^{3+} [7, 8].The C_{SP} values of the working electrode found by the CV curve using above equation 1. The calculated C_{SP} values are 139, 109, 75, 70 and 64 F g^{-1} for different scan rates from 10 to 100 mV s^{-1} respectively. The calculated C_{SP} values with corresponding scan rate are presented in table 1. The C_{SP} values are reduced with increase of scan rate. This is due to the ion (K^+) transfer process between electrolyte and electrode surface [10]. The maximum C_{SP} (= 139 F g^{-1}) is observed for $BiVO_4$ modified
electrode with the scan rate of 10 mV s^{-1}.

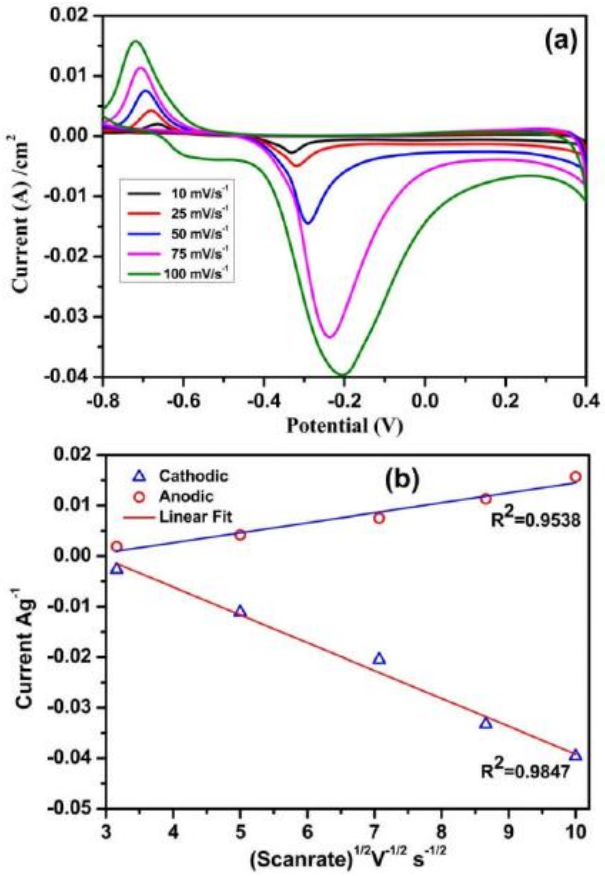

Fig.3. (a) Cyclic Voltamograme, (b) Peak current versus square root of scan rate plots of Monoclinic $BiVO_4$ sample

TABLE.1. SCAN RATE VS SPECIFIC CAPACITANCE

Sl.No	Scan rate	Specific capacitance (Fg^{-1})
1	10	139
2	25	109
3	50	75
4	75	70
5	100	64

IV. CONCLUSION

The flattened rice shaped $BiVO_4$ NPs were successfully prepared by sol-gel technique. From the structural analysis, the pure monoclinic $BiVO_4$ crystal structure was confirmed through PXRD pattern. The PXRD data sets were well matched with standard data. The surface morphology and sample purity were confirmed by SEM and EDX analysis. In addition the modified $BiVO_4$ NPs electrode was examined with cyclic voltametry analysis. Cyclic voltametry analysis showed the pseudocapacitance behaviour of $BiVO_4$ NPs. The electrode has obtained a maximum C_{SP} of 139 F g^{-1} at a scan rate 10 mV s^{-1}. These electrochemical study leads to flattened rice shaped $BiVO_4$ electrode is significant candidate for supercapacitor application.

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AUTHORS PROFILE

Dr. N. Nallamuthu has obtained his M.Phil. and Ph.D. physics in Pondicherry University, puducherry. Since 2012, he is working as an Associate Professor in Department of Physics, Kalasalingam Academy of Research and Education, Virudhunagar. His area of research mainly focused on solid state ionics, nanomaterials based energy devices. He has published ~20 research articles in reputed international journals.

R. Packiaraj is a Ph.D scholar at Kalasalingam Academy of Research and Education, India. His research interest is nanomaterials for electrochemical applications.

Dr. P. Devendran received his Ph.D degree in Physics from Madras University at Chennai in 2016, developing metal oxides and metal sulfide nano-catalysts for photocatalytic application. After he moved for postdoctoral studies at IRC, Kalasalingam academy of Research and education, he becomes an Assistant Professor of Physics at the same institution and presently began studying metal oxide modified graphene based materials for energy storage device application and their surface science. He published more than 28 research articles and book chapters in reputed journals.

Dr. S. Asath Bahadur is a Senior Professor in the Department of Physics, School of Advanced Sciences at Kalasalingam Academy of Research and Education, India. He has obtained Ph.D. in the area of X-ray crystallography from Madurai Kamaraj University in 1994 and also received his M.Phil. and M.Sc. Degree in physics from Madurai Kamaraj University.He has expertise in the areas of Crystallography and Material science. He has published more than eighty-fivepeer-review research articles in journals of international repute besides seventy more as proceedings.

K. S. Venkatesh received his Ph.D degree in physics from Alagappa University, karaikudi, India in the year of 2015. He obtained his M.Sc., degree in physics from Alagappa University, karaikudi india. He graduated from Madurai kamaraj university Madurai, India. He has 19 research publications in internationally peer reviewed journals. He has post doctoral research experience in Kalasalingam Academy of Resaerch and education, Krishnankoil,India. Currently, he is working as an assistant professor of Physice in Syed Ammal Arts and Science College, Ramanathapuram, India. His areas of research interests are Thin Films, Gas Sensors, and Supercapacitors.