Synthesis and Characterization of Sol-Gel Derived BIVO₄ Nanoparticles for Electrochemical Applications


Abstract: BiVO₄ 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 BiVO₄ NPs electrode was recorded by cyclic voltammetry (CV) in 2 M of KOH electrolyte. The enhance specific capacitance (Cₑₓ= 139 F g⁻¹) was observed at the scan rate of ~10 mVs⁻¹. The results show that the as synthesized BiVO₄ 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 for electrochemical energy storage devices have enlarged in

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(NO₃)₃·5H₂O and NH₄VO₃ 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 °C. The yellow sol was formed.
Further 1M of acetic acid (CH$_3$COOH) to make a 50 ml stock solution, the solution was added drop wise the solution maintained at 100 °C for a few hrs. The gel was collected and calcined at 600 °C 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 agreement 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.

![XRD pattern of Monoclinic BiVO$_4$](image)

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 ~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.

![SEM and EDX pattern of Monoclinic BiVO$_4$](image)

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 pseudocapacitance nature of the BiVO$_4$ sample. The faradaic redox reactions were take place on the surface of the electrode material.

\[
\text{BiVO}_4 + x\text{K}^+ + xe \leftrightarrow K_x\text{BiVO}_4\quad(1)
\]

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$^{2+}$. 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$^{-1}$.
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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REFERENCES


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