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Preparation of bismuth ferrite as photo-supercapacitive electrode

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Abstract. In this work, we report a novel concept of photo-assisted charging supercapacitive electrode of bismuth ferrite (BFO). The thin film layer of bismuth ferrite electrode is synthesized by electrodeposition technique. The effect of bismuth (III) nitrate/iron (III) nitrate ratio on the capacitive behavior of BFO electrode is investigated. FE-SEM demonstrates the morphology development of flake nanostructure of BFO at the equivalent ratio. The photo-supercapacitive electrode can deliver the highest specific capacitance of 220.50 F g^{-1} at 10 mV sec^{-1} under LED light irradiation which is higher than that obtained from dark conditions. This photo active layer can integrate function with the capacitive layer inducing photo-charging mechanism, thus it has great potential of this material electrode for photo-assisted charging supercapacitors application.

1. Introduction

Nowadays, there have been rapid developments in portable electronic devices and hybrid electric vehicles. Supercapacitors (SCs) are becoming the most attention as power energy supplies because of their high-power energy density, long life cycle, and fast charge/discharge system. Much effort has been devoted the materials for high-performance supercapacitors including transition metal oxides. Furthermore, the challenge to develop supercapacitors is not only to increase their electrochemical performance but also to elevate the function-level of supercapacitors by combining with others energy technology. Recently, the new concept is purposed as the photo-assisted charging supercapacitor devices, which directly integrate the system of harvesting and collecting energy in one electrode. Only a few reports attempted to develop electrode by using the photoactive/redox materials. Some materials classes of metal oxide such as Co(OH)_2 is purposed as photo-assisted charging supercapacitors. Its capacitive properties can gain the more charge transfer under blue light irradiation, but the capacitive efficiency is still not desire to achieve high power energy [1]. Bismuth ferrite (BFO) is one of promising semiconductor materials for supercapacitors with rhombohedral distorted perovskite structure. It has a narrow band gap between 2.3 and 2.8 eV with high chemical stability [2]. Theoretically, the synthesized nanoflake bismuth ferrite thin film via electrodeposition technique can yield the specific capacitance of 72.2 F g^{-1} at a current density of 1 A g^{-1} [3]. Moreover, bismuth ferrite



can be improved photocurrent response in photovoltaic applications [4]. Interestingly, this material classes reveal the multipotential efficiency for inducing charge redox reaction under the appropriate light energy. Also, the study of its photo-sensing inducing capacitive properties still has not been widely addressed. Thus, in the present study, the photoactive energy storage materials using bismuth ferrite (BFO) is purposed. The effect of bismuth (III) nitrate to iron (III) nitrate ratio on photo-electrocapacitive property is studied. Photo-assisted charging supercapacitors of BFO electrode is evaluated by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) under dark conditions and LED light irradiation.

2. Experimental section

2.1. Preparation of bismuth ferrite electrode

Bismuth ferrite thin films were electrodeposited on FTO substrate by applying voltage - 1.5 V for 900 second from the mixture aqueous electrolyte solution of 0.1 M bismuth (III) nitrate and 0.1 M Ferrite (III) nitrate at various ratio of 1:1, 1:2 and 2:1. The adding of 0.1 M tartaric acid solution was used to form complex substance and the aqueous NaOH is used to adjust pH. The various ratios of bismuth (III) nitrate to iron (III) nitrate at 1:1, 2:1 and 1:2 were named as BFO11, BFO21, BFO12, respectively.

2.2. Characterizations

The surface morphology of the samples was observed by field emission scanning electron microscope (FE-SEM, HITACHI SU-8010) at an acceleration voltage of 10 keV. The optical characteristics was examined using UV-Vis Spectrophotometer (LabTech BlueStar B).

2.3. Electrochemical measurements

To evaluate the electrochemical characteristics, cyclic voltammetry and galvanostatic charge/discharge were applied to conventional three-electrode configuration. The as-prepared samples, Ag/AgCl and platinum plate were used as working electrode, counter electrode and reference electrode, respectively. For cyclic voltammograms, the response current densities of the as-prepared electrode samples were recorded in 1.0 M KOH between -1.0 to -0.4 V (versus Ag/AgCl) from 10 to 100 mV/sec. The galvanostatic charge-discharge (GCD) of the as-prepared electrode samples were also recorded in 1.0 M KOH at current density range of 1 to 10 A g⁻¹ from -1.0 to -0.4 V with open circuit potential using PGSTAT 12 from 50 mHz to 10 KHz with alternate current amplitude of 5 mV. All the samples test was tested under dark conditions and LED light irradiation.

3. Results and discussion

The surface morphology of the as-prepared BFO electrode are investigated by field emission scanning electron microscopy (FE-SEM), as shown in fig. 1(a) - (c). Obviously, BFO surface demonstrates the development of flake structures depending on the ratio of Bi (NO₃)₃ to Fe (NO₃)₃. At Bi (NO₃)₃/Fe (NO₃)₃ ratio of 1 to 2, BFO reveals the typical structure of the dense flake morphology as seen in fig. 1(a). The increase the ratio of Bi (NO₃)₃ to Fe (NO₃)₃ up to 1 to 1 affects to increase the dense growth of anisotropic flake nanostructure surface as seen in fig.1(b). The presence of an aggregate irregular flake structures is observed as seen fig. 1(c) resulting from the increase Bi (NO₃)₃/Fe (NO₃)₃ ratio at 2 to 1, implying the trend of the occurring of the aggregate irregular shape with high content of Bi (NO₃)₃. Additionally, the energy dispersive X-ray spectroscopy (EDX) signal pattern of BFO11 electrode deposited onto FTO substrate is used to confirm the element surface of BFO11, consisting of Bi, Fe and O elements as displayed in fig. 1d. This presence of element ratio of Bi, Fe and O is identical close to the theoretical value of BFO. The optical properties of BFO11, BFO21 and BFO12 are characterized by UV-visible spectrophotometer as shown in Fig. 2. All BFO samples show the absorption spectra in the ultraviolet range, responding strongly in the range between 280 to 400 nm

and a sharp decline at wavelengths over 400 nm. Obviously, BFO11 shows the strongest optical absorption, expecting to possess the highest photocurrent response in photovoltaic applications.

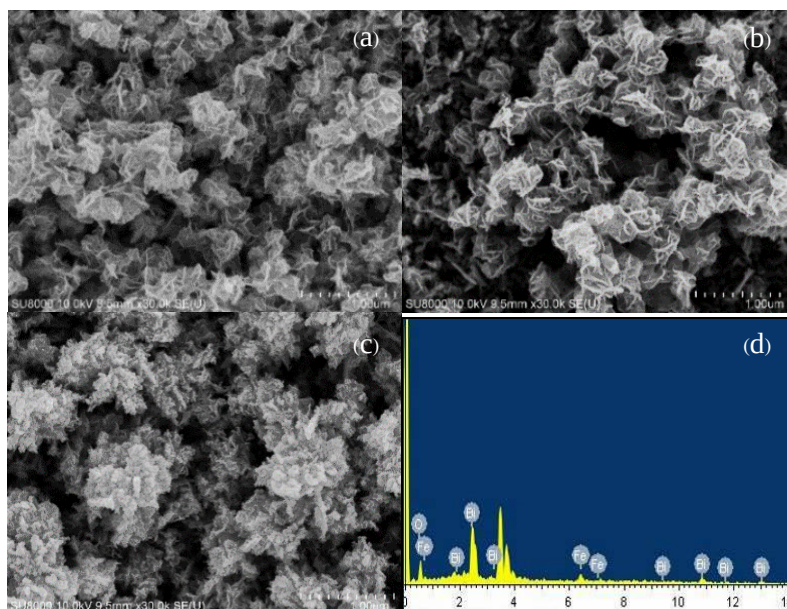


Figure 1. FE-SEM images of (a) BFO12, (b) BFO11, (c) BFO21 and (d) EDX spectra of BFO11

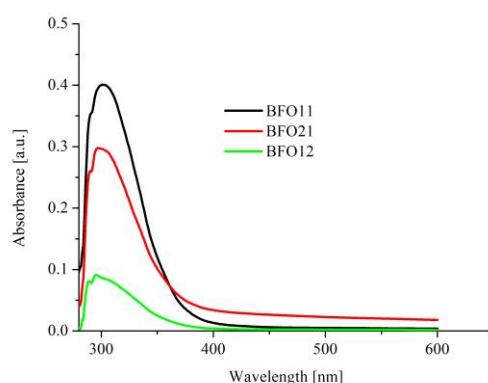


Figure 2. UV-Visible absorption spectra of BFO11, BFO21 and BFO12 samples

The electrochemical performance of BFO sample electrodes are evaluated using CV and GCD under dark condition and LED light irradiation. As seen in Fig. 3a and b, the electrodes of BFO11 displays the largest CVs area under both conditions than that obtained from BFO21 and BFO12 electrodes, indicating the highest activity. All GCD curves in fig. 3 c and d reveal an initial drop in the voltage during discharging owing to the internal resistances of low conductivity surface of BFO. The typical battery-like features and good pseudocapacitive behavior can be easily observed during discharge process. GCD results for all BFO electrodes are similar tendency with CV. BFO11 exhibits the longest discharge time under both conditions. Thus, it can be concluded that the optimum ratio of Bi (NO₃)₃/Fe (NO₃)₃ for the highest electrochemical performance under both dark and LED light condition is at ratio of 1 to 1. These results also correspond agreement with FE-SEM results supporting that the high active surface of flake structure of BFO11 can provide a facile shortcut path for charge transfer increasing a more efficient electrocapacitive properties [5]. The calculated specific capacitance values from GCD of the all as-prepared BFO electrodes under both conditions are showed as in fig 3e. BFO11 electrode under LED light can provide the more efficiency of 11% higher than

that obtain from dark condition (168.50 to 152.83 F g⁻¹). Interestingly, the increment of capacitance and current under LED light irradiation can occur from both the photo-charging mechanism and redox reaction. BFO is excited with LED light and then changed into the hole (h⁺) and electron pair (e⁻), thereby providing the more charge under LED light irradiation [6].

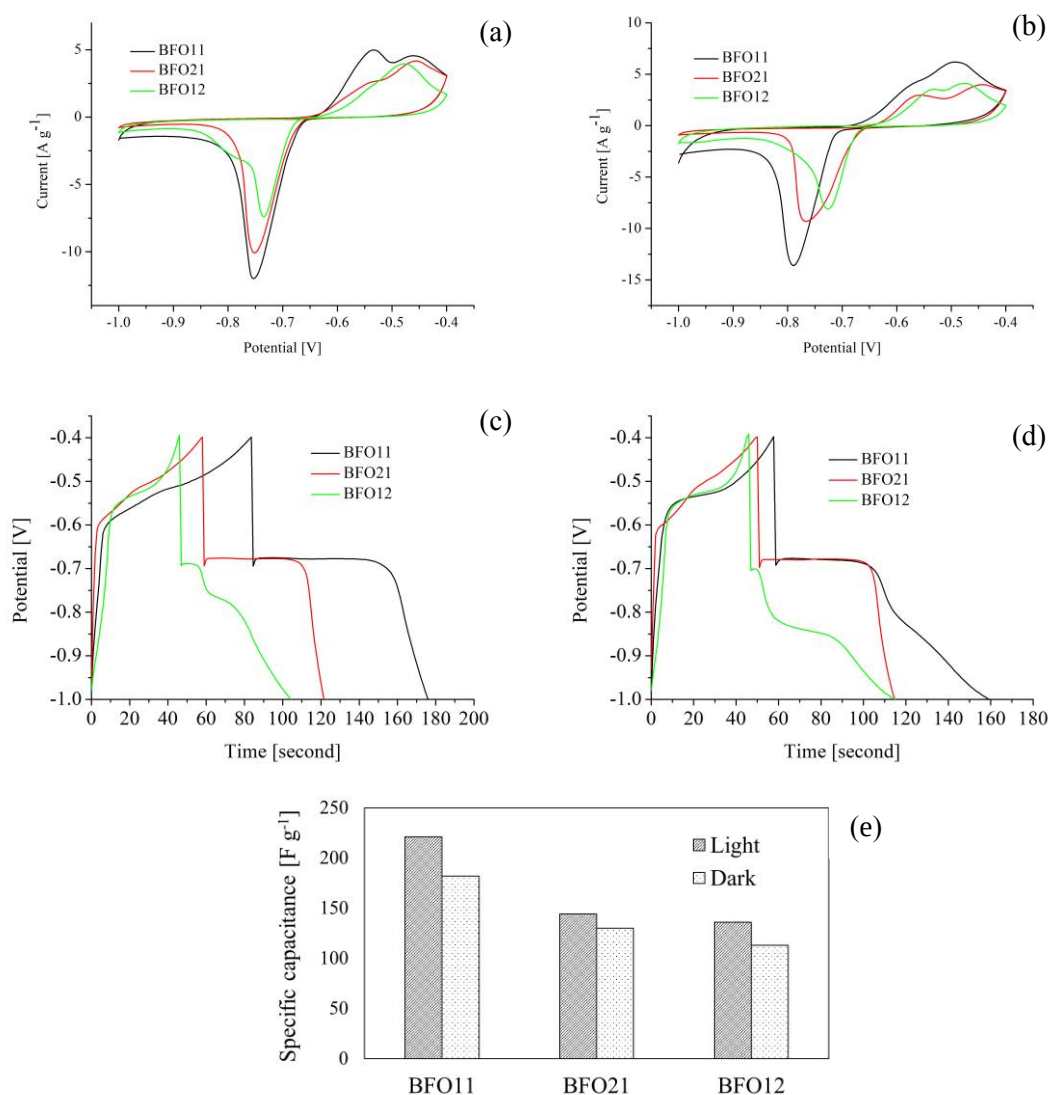


Figure 3. CV curves of various samples at 10 mV sec⁻¹ in 1.0 M KOH (a) under dark condition (b) under LED light irradiation; GCD curves of various samples at 1 A g⁻¹ in 1.0 M KOH (c) under dark condition (d) under LED light irradiation (e) specific capacitance of various samples at 10 mV sec⁻¹

The electrochemical performance of BFO11 electrode under dark and LED light irradiation at various scan rate is also evaluated as shown in fig. 4a and b. The good rate capability of BFO11 electrode with capacitance preservations around 31.07% (182.17 to 56.6 F g⁻¹) for dark condition and 32.27% (220.50 to 71.15 F g⁻¹) for LED light irradiation as the increasing of scan rate from 10 to 100 mV sec⁻¹, confirming that the better performance retention of BFO11 under LED light irradiation. GCD curve results of BFO11 under dark condition and LED light irradiation at various current densities also show the similar tendency results. The specific capacitance of BFO11 is 152.83 F g⁻¹ and 168.50 F g⁻¹ at 1 A g⁻¹ for dark condition and LED light irradiation, respectively. It can maintain the capacitance

preservations around 3.49% and 2.57% as current density from 1 to 10 A g⁻¹ under dark condition and the LED light irradiation, respectively.

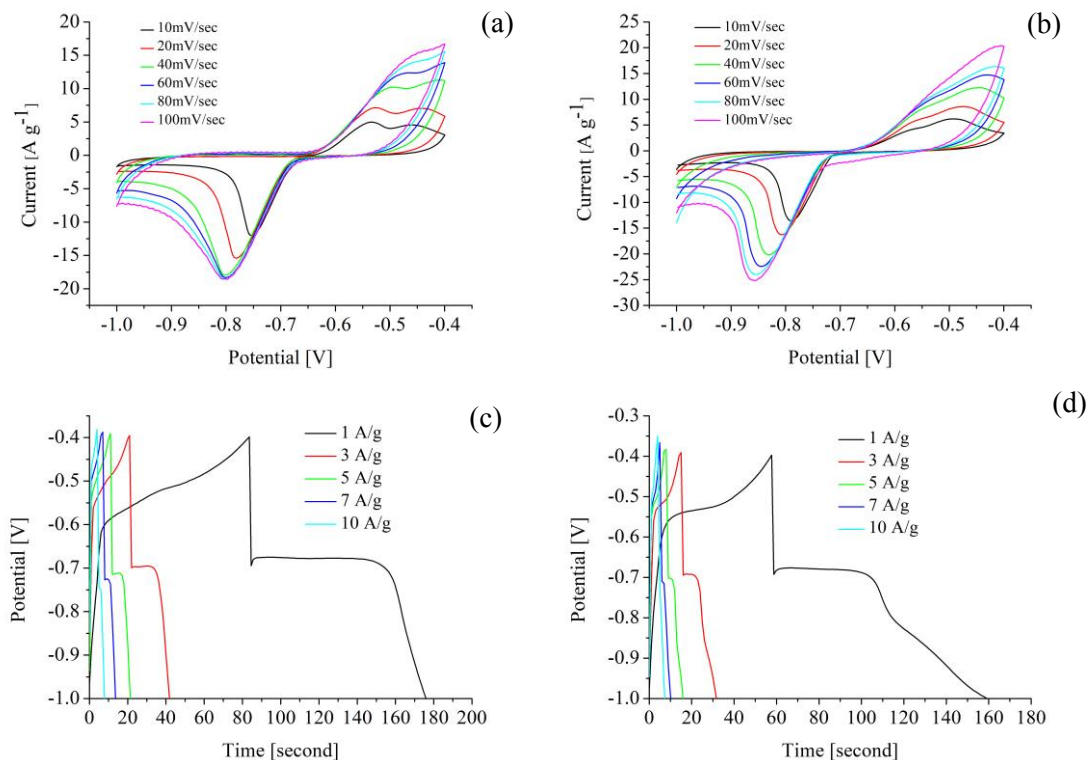


Figure 4. CV curves of BFO11 at different scan rates in 1.0 M KOH (a) under dark condition (b) under LED light irradiation; GCD curves of BFO11 at different current densities in 1.0 M KOH (c) under dark condition (d) under LED light irradiation

4. Conclusions

In summary, the as-electrodeposited bismuth ferrite with an equal ratio of bismuth (III) nitrate and iron (III) nitrate can provide the highest specific capacitance values under LED light irradiation due to the synergistic effects of pseudocapacitor mechanism and photo-charge generation mechanism of bismuth ferrite materials. This novel class material is purposed as charging photoactive supercapacitor and developed as promising materials for the next generation of photo-supercapacitor energy technology.

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