

Resistive Switching Property of Bmim(Br) Ionic Liquid under the Influence of ZnO Nanorods

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The majority of the research work in the area of resistive switching has been carried out with the help of organic, inorganic and hybrid materials. Only a few reports investigate resistive switching properties of ionic liquid and soft materials. In this report, we have synthesized ZnO nanorods (NRs) and Bmim(Br) ionic liquid using simple and low-temperature chemical route i.e., hydrothermal and reflux method, respectively. The structural study of ZnO NRs indicates that the formation of hexagonal crystal structure, evident from the XRD pattern. The FESEM image suggested the formation of nanorods like morphology. The effect of dispersed ZnO NRs on the resistive switching behavior of Bmim(Br) ionic liquid was studied. The study explains the change in switching behavior by dispersing the different concentrations of ZnO NRs in ionic liquid. The results demonstrated that the dispersed ZnO NRs in ionic liquid plays a vital role and will be a potential active switching material for resistive switching applications.

Keywords: ZnO, Nanorods, Ionic liquid, Chemical route, Resistive switching, Memristive effect.

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1. INTRODUCTION

The search for an excellent non-volatile memory device is currently pursued by academia and industry. Many potential candidates are being researched and developed in recent years that included but not limited to the phase change memory, flash memory, magneto-resistive memory, ferroelectric memory, and resistive memory. Among them, resistive memory is one of the preferred candidates for future memory storage applications. The resistive memory depends on the resistance change under the influence of electric stress; therefore, it promises many advantages over other counterparts such as low power consumption, high speed, and high density [1-2]. One of the device level artifacts of the resistive memory is a memristor or memristive device [3-4]. Apart from non-volatile memory, memristive devices also used for the development of synaptic devices [5] and sensors [6]. Given this, much research is currently underway to explore the memristive nature of various materials.

In order to find efficient memristive devices, various kinds of solid-state materials are being tested such as oxide [7], ferrite [8], biomaterials [9], and polymers [10]. On the other hand, few liquid-based systems also showed the memristive properties [11]. In the case of solid-state materials, zinc oxide (ZnO) is a propitious material for the memristive device due to its unique physical and chemical features. ZnO possesses excellent mechanical and thermal properties; therefore, it is an attractive material for electronic devices [12]. On account of the liquid system, the ionic liquid (IL) is an

exciting material and possess active electrical property, owing to inherent ions and ephemeral ion pairs [13]. Furthermore, ILs are regarded as a 'green solvent' and find many applications in the industry due to the excellent chemical and thermal stability [13].

In this contribution, we have synthesized ZnO nanorods (NRs) using the hydrothermal method, and the reflux method was employed for the synthesis of Bmim (Br) IL. The X-ray diffraction data (XRD) suggested the formation of a hexagonal crystal structure of the ZnO. We have dispersed the ZnO NRs in the Bmim(Br) IL and studied the resistive switching behavior of the ZnO NRs-Bmim(Br) IL system. For this, different concentrations of ZnO NRs dispersed in IL. The results indicate that the dispersed ZnO NRs in IL play an important role and show the memristive properties.

2. EXPERIMENTAL DETAILS

2.1 Materials

All the chemicals utilized in this work are analytical grade with high purity. Toluene, *n*-bromobutane, 1-methylimidazole, ethyl acetate, zinc acetate, ammonia solution, and deionized water were used for the synthesis of Bmim(Br) ionic liquid and ZnO NRs. All chemicals were used as it is, without any purification.

2.2 Synthesis of 1-butyl-3-methylimidazolium Bromide [Bmim][Br]

The synthesis of Bmim(Br) IL was carried out by a

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simple chemical route, as reported in the ref. [11]. In the typical process, an equimolar 1-methylimidazole and *n*-bromobutane were taken and mixed with toluene. The blend was refluxed at 80 °C for 48 h, freeze for 3 h and decanted the supernatant liquid from mixture. In addition to this, toluene traces from IL was removed by washing with ethyl acetate. The prepared Bmim(Br) IL was kept in the oven (low temperature) for 48 h to remove traces of ethyl acetate.

2.3 Synthesis of ZnO NRs

The hydrothermal method was used for the synthesis of ZnO NRs by varying growth temperature. At the outset, 1.09 g of zinc acetate was liquefied in 50 ml of distilled water, and ammonia was added dropwise under constant stirring until the formation of a precipitate. The beaker containing the end solution was kept in the autoclave at 90° for 2 h. After the reaction, a white solid product was collected and centrifuged at 9000 rpm for 15 min. Finally, it was annealed at 400° for 2 h. On a similar line, ZnO NRs were developed at various synthesis temperatures such as 100, 110 and 120°.

2.4 Dispersions of ZnO NRs in Ionic Liquid and Development of Devices

Dispersion of ZnO NRs in the Bmim(Br) IL was carried out by using an ultrasonic treatment. For the present study, different concentrations of ZnO NRs such as 0.05, 0.1, 0.5 and 1 wt. % were used. In the typical dispersion process, the desired amount of ZnO NRs and ionic liquid were inserted in a laboratory-grade tube. Furthermore, tubes suspended in the ultrasonic bath and treated for 1 hour at 80 W. Fig. 1 depicts the device assembly and experimental setup. We have followed the methodology reported in the ref. [11]. Here we have used symmetric thick copper electrodes as an anode and cathode (diameter: ~2 mm). The ArC ONE system was employed for the electrical measurements of the ZnO NRs-Bmim(Br) IL devices.

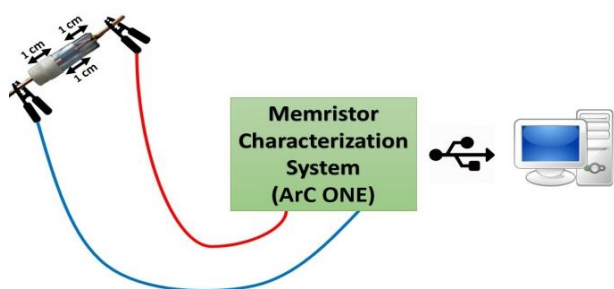


Fig. 1 – Device structure and measurement setup of the ZnO NRs-Bmim(Br) IL memristive devices

3. RESULTS AND DISCUSSION

The FESEM (MIRA3, TESCAN) was employed to investigate the morphology of the synthesized ZnO at 110° temperature. The low and high magnified FESEM images suggested that the well-ordered ZnO NRs were produced by the hydrothermal synthesis technique, as shown in Fig. 2a-b. The structural properties of the ZnO NRs were confirmed by XRD (D2 phaser, Bruker).

Fig. 3a-d represents the XRD spectra of the synthesized ZnO NRs. All characteristic peaks can be indexed to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3) and (1 1 2) diffraction planes and assigned to the 31.75°, 34.40°, 36.23°, 47.53°, 56.57°, 62.85° and 67.94° two theta angle. The intense peak of (1 0 1) suggested the formation of the hexagonal wurtzite structure. The ZnO NRs synthesized at 90, 100, 110 and 120° shows average crystallite size equals to the 38.56, 34.87, 54.79 and 48.64 nm, respectively. The results suggested that the ZnO NRs synthesized at 110 °C temperature shows better morphological and structural properties.

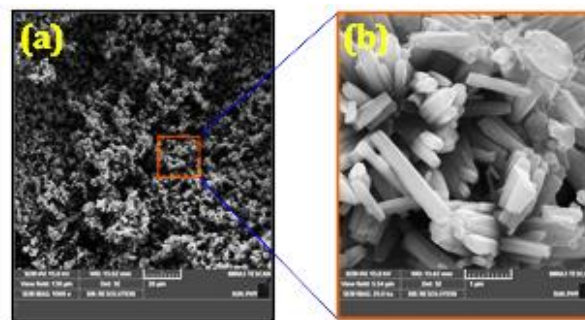


Fig. 2 – Low (a) and high magnification (b) FESEM images of the synthesized ZnO at 110 °C temperature

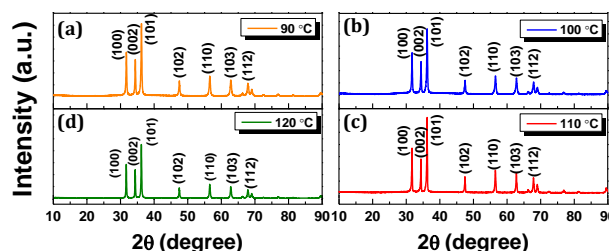


Fig. 3 – XRD spectra of the synthesized ZnO NRs at different temperature such as 90° (a), 100° (b), 110° (c), and 120° (d)

To understand the memristive switching effect within the device, the hysteresis loop in the current-voltage (*I-V*) plane is one of the critical criteria. In the present case, we have developed ZnO NRs-Bmim(Br) IL devices in the discrete form and investigated their memristive switching effects. In order to examine the ZnO NRs concentration effect on the memristive property of the Bmim(Br) IL, we have dispersed different concentrations of ZnO NRs in the Bmim(Br) IL such as 0.05, 0.1, 0.5 and 1 wt. %.

Fig. 4a-d represents the ZnO NRs concentration-dependent *I-V* characteristics of the Bmim(Br) IL devices. For each concentration study, four types of ZnO NRs, synthesized at different temperatures such as 90, 100, 110, and 120° were used. All devices show a hysteresis loop in the *I-V* plane along with non-zero crossing property. This suggested that the developed ZnO NRs-Bmim(Br) IL devices display the memristive switching effect [11, 14-15]. For all concentrations, the IL device based on 90° synthesized ZnO NRs shows poor memristive switching property than other devices. In the present case, the IL device based on 110° synthesized ZnO NRs shows good memristive switching property than other devices. On the other hand, the IL device based on 100° and 120° synthesized ZnO NRs shows moderate memristive switching property than other counterparts.

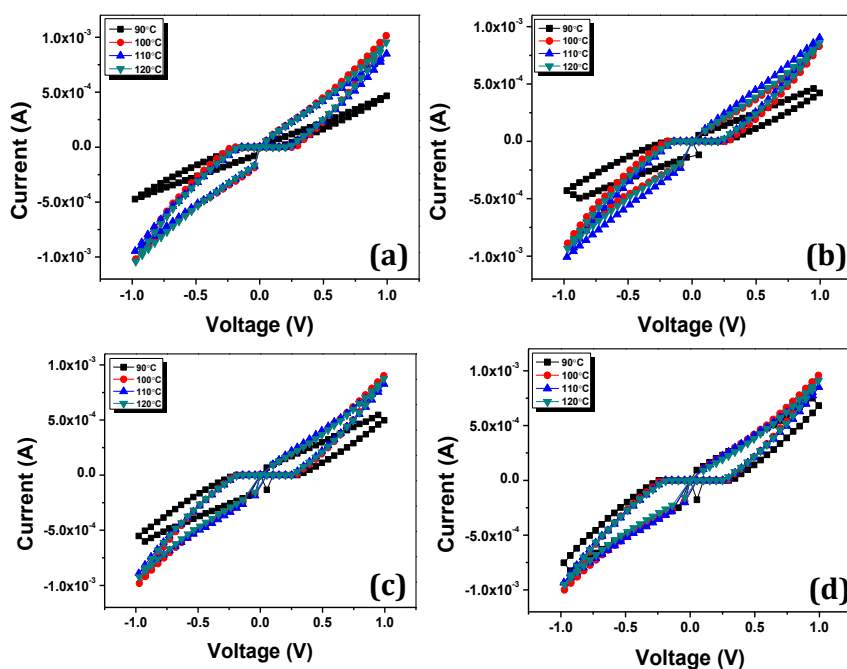


Fig. 4 – *I-V* characteristics of the ZnO NRs-Bmim(Br) IL devices. Various concentrations of ZnO NRs dispersed in the Bmim(Br) IL such as 0.05 wt. % (a), 0.1 wt. % (b), 0.5 wt. % (c), and 1 wt. % (d)

The hysteresis area is one of the crucial properties of the memristive devices. Fig. 5a represents the concentration and synthesis temperature-dependent hysteresis area of ZnO NRs-Bmim(Br) IL memristive devices. It is noticed that, as the concentration of the dispersed ZnO NRs in the IL increases, the hysteresis area tends to increase for 90° synthesized ZnO NRs. For other cases, the correlation of concentration of the dispersed ZnO NRs in the IL and the hysteresis area was not observed. However, ZnO NRs synthesized at 100, 110 and 120° show higher memristive hysteresis than 90° synthesized ZnO NRs. The 110° synthesized ZnO NRs show a good memristive hysteresis area than other devices. In particular, 0.1 wt. % (at 110°) ZnO NRs shows a good memristive hysteresis area than other devices. The endurance of cyclic switching of the ZnO NRs-Bmim(Br) IL memristive devices (Fig. 5b). The bi-level switching from low resistance state (LRS) to high resistance state (HRS) and vice versa were detected for all devices. Furthermore, good endurance switching over 10^3 cycles were observed for all devices, suggesting the good reliability of the device. Because of this, developed ZnO NRs-Bmim(Br) IL-based discrete memristive devices can be useful for the various applications.

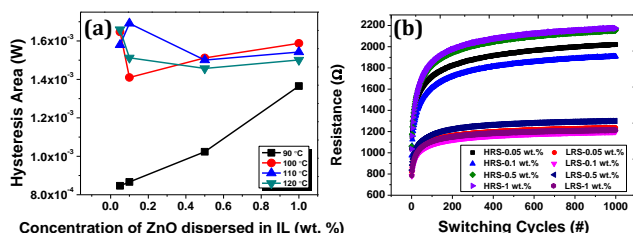


Fig. 5 – Concentration of ZnO NRs dependent a memristive hysteresis area (a) and endurance property (b) of 110° synthesized ZnO NRs-Bmim(Br) IL memristive devices

4. CONCLUSION

The ZnO NRs and Bmim(Br) ionic liquid were synthesized by using simple chemical routes i.e. hydrothermal and reflux method, respectively. In this work, ZnO NRs were developed at various synthesis temperatures such as 90, 100, 110 and 120 °C. Furthermore, different concentration ZnO NRs such as 0.05, 0.1, 0.5 and 1 wt. % were dispersed in the IL and investigated their memristive switching property. The XRD spectra suggested the formation of a hexagonal crystal structure. The FESEM image suggested the formation of nanorods like morphology. The effect of dispersed ZnO NRs on the resistive switching behavior of Bmim(Br) ionic liquid was studied. The hysteresis loop along with non-zero crossing property, was observed for all the memristive devices. In the present case, 110 °C synthesized ZnO NRs with 0.1 wt. % shows good memristive switching property than other devices. The endurance test suggested that all devices show bi-level switching from LRS to HRS and vice versa. Furthermore, good endurance switching over 10³ cycles were observed for all devices, suggesting the good reliability of the developed devices.

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