

SUSTAINABLE PRODUCTION OF GRAPHENE OXIDE AND ZINC OXIDE NANOPARTICLES FROM SPENT Zn-C BATTERIES

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ABSTRACT – Recycling batteries helps to reduce waste, protects the environment, and allows their components to be reused in the manufacture of new products. In this work, the possibility of valorizing zinc and graphite from spent Zn-C batteries was investigated, not only to reduce pollution but also to create new materials with a wide range of industrial applications. Graphite electrodes were used for the synthesis of graphene oxide (GO) by the modified Hummer's method, while zinc was used for the synthesis of zinc oxide nanoparticles (ZnO-NP) by the coprecipitation method. The synthesized GO and ZnO-NP were structurally analyzed by X-ray diffraction (XRD). The appearance of a new diffraction peak at 10.7° and the decrease in the intensity of the diffraction peak of graphite at 26.6° and 42.4° indicate the oxidation of graphite and the formation of graphene oxide. In the case of the XRD pattern of ZnO, zincite was identified as the only crystalline phase, and the average crystal size was 41.63 nm.

Keywords: Recycling, Zn-C batteries, Zinc oxide, Graphene oxide.

INTRODUCTION

Zinc-carbon (Zn-C) batteries are the primary cells [1] used in numerous portable electronic devices worldwide due to their low cost, good durability and simple production technology [2,3]. The Zn-C battery contains graphite as the cathode, a mixture of manganese dioxide and carbon moistured with NH₄Cl/KCl as the electrolyte and a zinc container as the anode [4]. Since spent Zn-C batteries cannot be recharged and their proper storage is very expensive, spent Zn-C batteries are usually disposed of directly in landfills [5]. The improper disposal of Zn-C batteries in the environment not only leads to waste of Zn, Mn and C resources [6], but also to environmental pollution [3,7]. Recently, numerous research teams have focused their attention on recycling Zn-C batteries as an optimal solution to reduce the amount of waste, protect natural resources, the environment and human health [1,3-5,8].

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By recycling Zn-C batteries, the individual components can be effectively separated and reused in the synthesis of new products [3]. Zinc from spent Zn-C batteries can be used for the synthesis of ZnO nanoparticles [8], which are widely used in photocatalytic processes [9], in the production of gas sensors with high physical and chemical stability [10], solar cells [11], etc. Graphite from spent Zn-C batteries can be used as a precursor for the synthesis of graphene oxide [5]. Graphene oxide is widely used in wastewater treatment [7], but also for the modification of photocatalysts [12], membranes [13], sensors [14], etc. Regeneration of the electrolyte of Zn-C batteries enables the synthesis of valuable compounds, including ammonium zinc orthophosphate and manganese(IV) oxide. Manganese(IV) oxide has significant potential for use in the production of new batteries or as a catalyst in various oxidation processes. Ammonium zinc orthophosphate can be reused as a microfertilizer and offers an environmentally friendly solution for agricultural practice [2].

The aim of this study is to explore the recycling potential of spent Zn-C batteries, focusing on the recovery of zinc and graphite and the synthesis of valuable materials such as ZnO-NP and GO.

EXPERIMENTAL

Materials

Spent Zn-C batteries (Batt Extra Life, Standard Line, size AAA, 1.5 V) were collected from various battery-operated electronic devices. Hydrochloric acid, sulfuric acid, sodium hydroxide, sodium nitrate, potassium permanganate and hydrogen peroxide were also used for the purpose of this study. All chemicals were of analytical grade and were used without further purification.

Disassembly of Zn-C batteries into their individual parts

Zn-C batteries without visible external damage were collected for the laboratory tests. The Zn-C batteries consisted of a plastic case, metal terminals, a zinc anode container, a plastic and paper insulator, electrolyte, and a graphite electrode (Figure 1). When opening the Zn-C batteries, the plastic casing was removed first and then the metal terminals were removed. In the next step, the batteries were carefully opened and the anode material was separated from the cathode material, the electrolyte, and the insulators. The graphite electrode was then carefully removed from the electrolyte and the electrolyte was separated from the paper insulator using a spatula.



Figure 1 Zn-C batteries and their individual parts

Synthesis of ZnO nanoparticles

The zinc from spent Zn-C batteries was polished, washed with distilled water, and treated in an ultrasonic bath for 15 minutes. According to Das et al. [15], 2 g of zinc was dissolved in 20 ml of HCl at a temperature of 80°C with constant stirring on a magnetic stirrer. 1M NaOH solution was slowly added to the formed zinc solution to carry out the precipitation process. The solution was filtered and the separated precipitate was dried in an oven until it was dry and then calcined at a temperature of 600°C for 3 hours to form ZnO.

Synthesis of graphene oxide

Graphene oxide was synthesized by a modified Hummer's method [16,17]. The graphite electrode separated from the Zn-C batteries was polished with sandpaper and then treated with HCl to remove any remaining dry electrolyte. The electrode was then dried in an oven and ground in a mill. 1.0 g graphite powder, 1.0 g sodium nitrate, and 50 ml sulphuric acid were mixed in a laboratory beaker. The laboratory beaker was placed in a home-made ice bath with a magnetic stirrer. KMnO_4 was then gradually added to the reaction mixture and the system was stirred for one hour to allow the manganese oxidation reaction and graphite salt formation to take place. After one hour, approximately 500 ml of distilled water and 15 ml of H_2O_2 were added to the reaction mixture. The reaction mixture was then filtered and the separated precipitate was dried in an oven at 80°C.

Characterization methods

The structure and crystallinity of the ZnO and GO samples were analysed by X-ray diffraction (XRD). XRD analysis was performed using a RigakuMiniFlex 600 instrument with a D/teXUltra 250 high-speed detector and X-ray tube with a copper anode. The imaging conditions were: Angular range 3-90°, scanning speed 10°/min. The voltage of the X-ray tube was 40 kV and the current 15 mA. Mineral identification was performed using PDXL 2 software version 2.4.2.0 and the obtained diffractograms were compared with data from the ICDD PDF-2 2015 database.

RESULTS AND DISCUSSION

Characterization of ZnO nanoparticles

The diffractogram of the ZnO samples is shown in Figure 2 and shows that zincite was identified as the major crystalline phase in the analyzed sample. The diffraction peaks identified at 31.80°, 34.45°, 36.29°, 47.59°, 56.65°, 62.92°, 66.45°, 68.02°, 69.16°, 72.64°, 77.04°, 81.48° and 89.72° are identical to those from the ICDD PDF-2 2015 database (Card No. 01-082-9744) and confirm a hexagonal wurtzite phase of ZnO. The crystal lattice parameters (a and c) of the hexagonal wurtzite structure are 3.25 and 5.2, respectively, and correspond to the values of the reference sample [8].

The Debye-Scherrer formula was used to determine the average crystal size of ZnO nanoparticles [9]:

$$D = \frac{k \cdot \lambda}{\beta \cdot \cos \theta} \quad (1)$$

Where D is the crystallite size (nm), k is the constant (0.89), λ is the wavelength of the X-rays (0.154 nm), β is the full width at half maximum of the most intense diffraction peak (FWHM) (rad) and θ is the Bragg angle ($^{\circ}$). The average crystal size of the ZnO nanoparticles was determined by measuring the FWHM of the most intense peak and amounted to 41.63 nm.

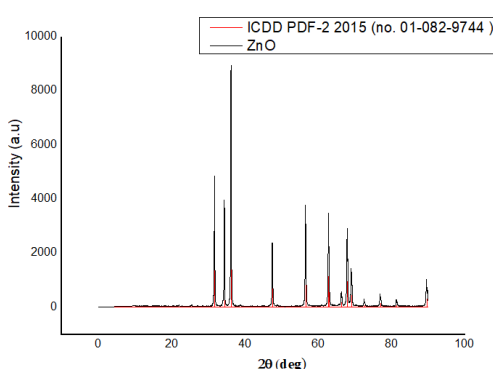


Figure 2 Diffractogram of ZnO nanoparticles

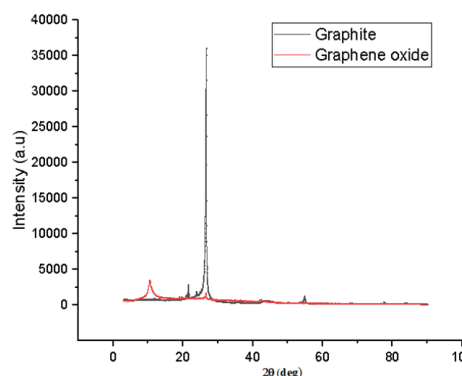


Figure 3 Diffractogram of graphite obtained from spent Zn-C batteries and synthesized GO

Characterization of GO

XRD analysis was used to investigate the conversion of graphite from Zn-C batteries into GO. The diffractograms of the initial graphite powder from Zn-C batteries and the synthesized graphene oxide are shown in Figure 3. The characteristic graphite peaks were observed at 26.6° , 42.4° , and 54.7° and attributed to the basal planes of graphite (002), (100), and (004), respectively. Similar results were obtained by Loudiki et al. [16], Silva et al. [17] and Sperando et al. [18]. A sharp diffraction peak at 26.78° of the basal reflection plane (002) indicates a highly crystalline hexagonal structure of the graphite powder [16,18]. A small peak at 21.4° may indicate the presence of impurities [16]. However, it is not possible to identify an impurity from a single diffraction peak.

In the case of the XRD pattern obtained for GO, a new peak at 10.7° was observed, indicating the presence of graphene oxide and corresponding to the (001) diffraction plane [12,17,19]. In addition, residual peaks of graphite at 26.6° and 42.4° were observed, but their intensity is significantly lower than that of the initial graphite, suggesting that graphite was exfoliated to obtain GO layers. Similar results were obtained by Silva et al., [17].

CONCLUSION

Recycling Zn-C batteries is a sustainable solution to reduce landfill waste, protect the environment and preserve human health. For this reason, the potential of valorizing Zn and C from spent batteries and reusing them for the synthesis of ZnO nanoparticles and

GO was investigated in this work. XRD analysis confirmed the formation of ZnO-NP with a hexagonal wurtzite structure and the successful conversion of graphite to graphene oxide.

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