Preparation of Graphene-based Conductive Ink from Spent Zinc-carbon Batteries

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Demands for batteries have been increasing each year globally. This results in an enormous number of waste batteries, especially non-rechargeable types. It can pose severe environmental and health hazards if disposed of improperly. The consumers are generally not aware of how waste batteries should be properly disposed, thus, they usually end up in landfills worsening its risks. Hence, determining a more valuable alternative usage is a sustainable solution. In this study, graphite rods from the waste primary (zinc-carbon) batteries were utilized to produce conductive ink. Graphite rods were systematically removed from the spent batteries, cleaned with acetone to remove the plastic coating, and dried. It was then electrochemically exfoliated by applying 10 V and 2 A while submerged in an H2SO4 solution (1 M). The resulting powders were filtered, rinsed with distilled water until neutral pH, and oven-dried (80°C). These were then dispersed in silver-ammonia solution and hydrothermally reacted at 150°C for 5 h. Sodium silicate solution was used as a dispersing medium for the reduced graphene oxide (rGO) powder producing conductive ink. The ink demonstrated a good surface adhesivity, very low resistivity (<30 μΩ·m), and consistent even after 500 bending cycles. Also, Ag@rGO powder’s morphology, surface characteristics, and physicochemical properties have been evaluated using XRD, Raman, and FE-SEM.

Key Words
Graphene, Conductive ink, Spent batteries

1. Introduction
Manufacturing circuit boards traditionally involve many steps, such as etching and electroplating. However, it is time consuming, expensive and the solvent used in the etching process is very corrosive and dangerous 1). Hence, the increasing demand for environmentally benign processes. One alternative is the use of conductive ink in various electrical applications. However, the challenge is to maintain stable electrical conductivity with compatibility to its adhering surface. Using graphene can mitigate this difficulty.

Graphene is extremely useful for fundamental studies and in a wide range of electrical and electronics applications. Graphene is synthesized from graphite sources where graphene layers are exfoliated in various processes 1). Traditional techniques are Hummer’s method to produce graphene oxide with a further reduction to graphene or through direct solvent exfoliation of graphite 2). Graphene charge carriers are massless particles or Dirac fermions at ambient condition; hence, it has good applicability for printing and coating 3). Graphene has been increasingly studied for its application in printed electronics, conductive coatings, inks, composite fillers, solar cells, sensors, lithium-ion batteries, and supercapacitors 3). Conductive ink arises to these applications providing a low-cost and scalable method for its production with a high rating for printing 3). This ink has obtained many different physical properties, including the concentration of fillers present, non-wettability, and resistance persisting up to ~300,000 cycles at 3% bending.
The utilization of graphene in ink form can achieve fabrication with high-performance, stable, low-cost, and zero-waste of materials.

Graphene ink can be synthesized from any graphite source in pristine form or waste materials like batteries. Primary batteries typically consist of anode, cathode, electrolyte, separators, and carbon graphite rod. These are highly disposable and are widely present in every household. In the United States of America (USA), batteries are estimated to be a US$ 2.5 billion industry with annual sales of nearly 3 billion cells, which can become part of the waste stream. Reuse and proper management of these waste batteries are needed because the world is highly reliant on this technology. Billions of waste batteries (especially zinc-carbon batteries) should be collected and recycled, and one alternate is graphene production, which can be processed to ink and other forms of applications.

In this study, the carbon graphite rod of a primary non-rechargeable battery (zinc-carbon) was electrochemically exfoliated to produce bulk partially oxidized graphene. It was then doped with silver (<5 wt. % Ag) via hydrothermal reaction. Sodium silicate solution (2:3 H2O v/v) was used as a dispersing medium to produce conductive ink. The electrical and mechanical properties of the conductive ink tracks on paper were determined. Furthermore, a basic demonstration of the applicability of the as-produced conductive ink was shown by preparing paper-based electronics. This study successfully demonstrates an upcycling route for handling waste batteries.

2. Experimental

2.1 Materials

Graphite rods from zinc-carbon batteries were used as the precursor for the preparation of reduced graphene oxide (rGO). Sulfuric acid (98% H2SO4, RCI Labscan Ltd.) was used for the preparation of electrolyte for electrochemical exfoliation. Silver nitrate (≥99.0% AgNO3, Aldrich USA) and ammonia solution (25% NH3, Merck Germany) were used to dope silver to graphene. Sodium silicate (Technical grade, Chemline) was used for the conductive ink preparation.

2.2 Synthesis of partially oxidized graphene (pOG)

Prior to the start of the reaction, graphite rods were systematically removed from the spent batteries, cleaned with acetone to remove the plastic coating, and dried. Graphite rod, copper wires, and 1 M H2SO4 solutions were used as working electrodes, counter-electrodes, and electrolytes, respectively. A positive voltage of 10 V and 1 A current was applied to the graphite electrode for 0.5 h. The exfoliated graphite powder was filtered, washed with distilled water until neutral pH, and dried at 80°C for 12 h.

2.3 Synthesis of silver-coated rGO (Ag@rGO) composite

AgNO3 (0.1 M, 20 mL) solution was added with ammonia until brown precipitates were gone, and the solution became colorless. The silver-ammonia [Ag(NH3)2OH] solution was mixed with pOG (1 g) and stirred for 30 minutes. The solution was then transferred to a Teflon-lined stainless-steel autoclave reactor and heated at 150°C for five h. After cooling down to room temperature, the solution was filtered, washed with distilled water, and oven-dried at 80°C for 12 h.

2.4 Conductive ink preparation

Sodium silicate solution was mixed with distilled water (2:3 vol. ratio) and sonicated for 1 h. Conductive powder (Ag@rGO) was dispersed to the prepared solution by sonication for 1 h to produce homogeneous ink.

2.5 Resistivity Measurement

Conductive inks were used to draw lines to a white bond paper (80 g m⁻²) and dried at room temperature for 2 h. Four-point probe method was used to measure the line resistance of the drawn conductive ink. Electrical resistivity (Ω) was calculated using Eq. (1), where R is the resistance, l is the length, and A is the cross-sectional area of the line.

\[ \Omega = \frac{RA}{l} \]

2.6 Surface adhesion test

The surface adhesion test was based on the American standard test method (ASTM) D 3359-97, known as the cross-cut tape test. Briefly, a lattice pattern with six cuts in each direction was made in the film to the substrate. A pressure-sensitive tape was applied over the pattern and then removed. Adhesion will be evaluated by comparison with the description and illustration of the suggested scale.

2.7 Characterization

The structural property and identity of the conductive powder were determined via X-ray diffraction (XRD) analysis (40 kV, 40 mA, 0.03 step count⁻¹, Cu Kα source, Rigaku Smartlab) and Raman analysis (laser frequency of 532 nm, 2.33 eV, DXR Raman system, Thermo Fisher Scientific, America). Morphology of the synthesized products were examined using Scanning Electron Microscope (SEM-EDX, Hitachi S-3500 N, Japan).
3. Results and Discussion

3.1 Mechanism

Ag@rGO composite was prepared following a two-step method (Fig. 1). Graphite rods from spent batteries were electrochemically exfoliated, and the as-produced pOG was doped with Ag via hydrothermal reaction.

The mechanism of electrochemical exfoliation of the pOG (Fig. 2) starts when an applied voltage enables the ionic species to intercalate into the graphite rod. The defective sites at the edges or grain boundaries begin to open, allowing migration of sulfate (SO$_4^{2-}$) and water (H$_2$O) molecules, eventually releasing localized gas bubbles (SO$_2$, O$_2$). Hence, this leads to the expansion of the interlayer distance of graphite exfoliating graphene sheets and causing it to be partially oxidized. Then, the produced bulk pOG powder was coated with Ag in its sheets via hydrothermal reaction to produce Ag@rGO conductive powder.

3.2 Conductive powder characterization

The Ag@rGO composite showed a sheet-like morphology with some particles spread throughout its surface (Fig. 3 a). The same feature was observed when the conductive powder was dispersed in the sodium silicate solution and hand-painted in a paper substrate (Fig. 3 b). Fibers from the paper substrate cannot be observed evidently, showing that it was fully coated with the conductive ink. The XRD pattern showed faint peaks (Fig. 4 b) belonging to Ag, signifying that only very little...
amount of Ag was doped in the composite. Nevertheless, the composite became more crystalline, as shown by the sharpened peak at ~24° of the composite (Ag@rGO) compared to electrochemically exfoliated graphene (EG) 16,17. On the other hand, Raman analysis revealed a slight enhancement of the D (1346 cm⁻¹) and G (1585 cm⁻¹) bands with the presence of the Ag particles arising from the electromagnetic mechanism effect based on the charge transfer between graphene and Ag 18. Furthermore, the presence of 2D band (2685 cm⁻¹) and the intensity of G band higher than D band are typical for multilayer graphene sheets 19,20.

3.3 Electrical and mechanical properties of conductive ink

The as-produced Ag@rGO powder was dispersed in sodium silicate solution and sonicated to produce a homogeneous conductive ink, which was then used to draw tracks in a paper. The effect of solid to liquid ratio (S L⁻¹) was investigated by varying the loaded conductive powder in the solution. For comparison and control, the conductive powder produced directly from pristine graphite rods of unused batteries was also tested. As the S L⁻¹ ratio increased, the resistivity lowered for both types as caused by the presence of more conductive powder (Fig. 5). However, when S L⁻¹ was further increased to 0.7, a slight increase in the resistivity was observed, which can be caused by too much powder non-homogeneously dispersed in the solution. Nevertheless, the ~1.5 x 10⁻⁵ Ω·m resistivity is already significantly low enough for the electronic application of the conductive ink 21,22. This is especially significant since sintering (>120 °C) to enhance particle connectivity, thereby lowering resistivity 21, was not used in this study. Furthermore, the conductive powder from unused batteries showed slightly higher conductivity but the difference is not significant validating the use of graphite rods from spent batteries.

The conductive ink tracks also showed excellent mechanical flexibility (Fig. 6). The paper with drawn tracks was bent at ~90° (Fig. 6 a), and electrical resistivity was measured before and after bending (Fig. 6 b). The resistivity did not significantly change even after 500 bending cycles. Although at S L⁻¹ = 0.2 g mL⁻¹, resistivity increased at bending cycles >300, which can be attributed to loosening of the particle connectivity after several bending.

Furthermore, the conductive ink has an excellent adhesivity as no flaking (ASTM D3359-97) was observed even after applying a pressure-sensitive tape on the lattice patterns, thereby validating the suitability of sodium silicate as a binder and dispersing medium for the conductive powder.
3.4 Paper-based electronic application

A simple electronic circuit was drawn on a paper (Fig. 7) to demonstrate the applicability of the conductive ink for writing electronics. A light-emitting diode (LED) was mounted on the surface of the drawn tracks between the gaps. Upon application of 3 V using a regulated power supply (MCP, M10-QD305), the LED illuminated and functioned well with very low circuit loss. This validates that the drawn electronic circuit using the as-prepared conductive ink has significantly low resistivity. Hence, further demonstrating the graphene-based conductive ink can be used in other complicated electronic circuit applications showing good flexibility and excellent adhesivity.

4. Conclusion

Graphite rods from spent zinc-carbon batteries were successfully utilized to produce electrochemically exfoliated graphene, which was then doped with Ag. The Ag@rGO powder was homogeneously dispersed in sodium silicate solution to produce the conductive ink. The drawn tracks of the ink in the paper substrate has significantly low resistivity (< 3.5 x 10^-5 Ωm) and maintained this even after 500 bending cycles. The applicability of the conductive ink for paper-based electronics was also shown with the use of a 3V rated LED light functioning well. This indicates that the application of the conductive ink more complicated flexible electronic circuits using different substrates can further be explored. Also, the prepared graphene-based conductive ink is a very sustainable upcycling route for handling spent batteries, finding value, and repurposing of waste.

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