



# A low-cost non-conjugated dicarboxylate coupled with reduced graphene oxide for stable sodium-organic batteries



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## HIGHLIGHTS

- Newly designed organic electrode using cost-effective, green sodium humate.
- Na-storage processes studied by ex-situ characterizations and DFT calculations.
- The hybrid sodium humate/rGO electrodes achieves highly revisable sodium-storage activity.

## ARTICLE INFO

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## ABSTRACT

Eco-efficient and renewable organic electrodes are considered to be a promising alternative for upcoming large-scale applications of low-cost energy storage systems. Here we report that cost-effective and green sodium humate (Na<sub>2</sub>HA) with non-conjugated carboxylate groups, can serve as a highly reversible anode material for sodium-organic batteries. Functionalized by reduced graphene oxide (rGO), the hybrid electrode delivers a highly reversible discharge capacity of 133 mAh g<sup>-1</sup> at a current density of 500 mA g<sup>-1</sup>, achieving a capacity retention of 91.6% over 2000 cycles. The Na-cycling mechanism in Na<sub>2</sub>HA is proposed. Density functional theory calculations demonstrate that the low energy barriers for Na-ion insertion/extraction in Na<sub>2</sub>HA facilitate the charge transfer. Such findings may offer new possibilities for designing and enlarging eco-efficient and renewable organic compounds for sodium-organic batteries.

## 1. Introduction

Small organic carbonyl molecules serving as electrode materials have recently attracted much interest in electrochemical energy storage systems because of their renewability, environmental friendliness, designability, diversity, and definiteness of structures [1–7]. However, several drawbacks, especially serious dissolution into the electrolyte and intrinsic low electrical conductivity, remain to be addressed for practical applications [8–10]. Considerable efforts have been made to restrain the dissolution through the electrostatic interactions,  $\pi$ - $\pi$  interaction effect, hydrogen-bonding interactions, covalent bonds, and physical barrier [11–27]. Combining organic materials with carbon materials or conducting polymers, or designing molecular structures with narrow band gaps are effective strategies to improve the electrical conductivity of organic electrodes [28–33]. Generally, electrode materials for sodium-ion batteries (SIBs) should be resourceful and possess

outstanding cyclability even at a high rate, while the graphite usually for lithium-ion batteries (LIBs) cannot work efficiently for SIBs [34–36]. More importantly, the previously reported small organic carbonyl molecules often comprise conjugated structures like benzene rings and naphthalene rings, whereby conjugated moieties stabilize the enolic structures, achieving remarkable electrochemical performances [37–39]. Nevertheless, the variety of conjugated carbonyl-containing small organic molecules is small, and thus the screening of conjugated carbonyl-containing organic electrodes is limited. It is highly desirable to develop non-conjugated carbonyl-containing electrodes through eco-efficient processes for high-performance sodium-organic batteries.

In this work, we report for the first time that low-cost and environmentally friendly sodium humate (Na<sub>2</sub>HA, Scheme 1) comprising non-conjugated carbonyl groups can serve as a SIB anode material. It is known that Na<sub>2</sub>HA, generally extracted from leonardite, has versatile capabilities for adsorption, exchange, complexation, and chelating

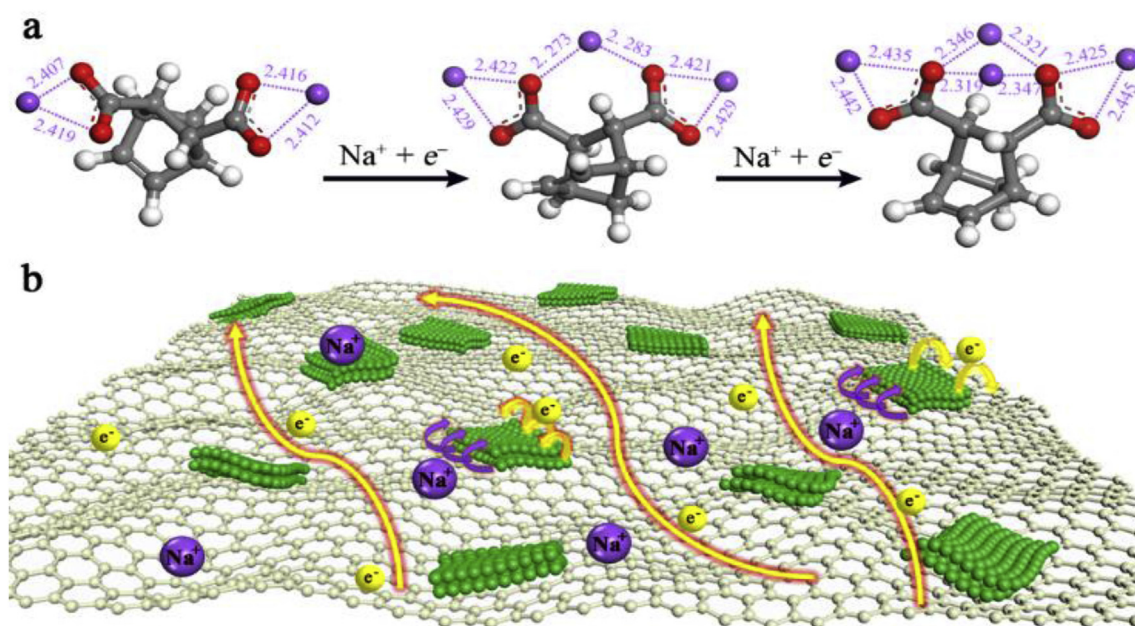
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**Scheme 1.** (a) Molecular structures of  $\text{Na}_2\text{HA}$  inserted with different numbers of  $\text{Na}^+$  ions. Na, O, C, and H atoms are denoted in the color of purple, red, gray, and white, respectively. The unit for the distance between atoms: Å; (b) Schematic illustration for the charge transfer in the hybrid  $\text{Na}_2\text{HA}/\text{rGO}$  electrode.

applications because of its abundant reactive groups [40]. Also, humate acid is available in abundance and widely exists in nature. It is largely derived from the metabolites of microorganism-decomposed remains of animals and plants, and able to transform into  $\text{Na}_2\text{HA}$  [41]. Herein, the unique electrode made of  $\text{Na}_2\text{HA}$  functionalized by reduced graphene oxide (rGO) exhibits outstanding sodium storage performances. The electrochemical reaction processes of Na-ion insertion/extraction in  $\text{Na}_2\text{HA}$  are explored by experimental and theoretical analyses. This research may provide new possibilities and insight into organic electrode materials without conventional conjugated groups for sodium storage applications.

## 2. Experimental

### 2.1. Preparation of electrode materials

The commercially available powder of  $\text{Na}_2\text{HA}$  (99.97%, Aladdin) was directly used in this work. The graphene oxide (GO) suspension was prepared according to the modified hummer's method. The Raman spectrum (Fig. S1) and the detailed preparation process for GO are described in Supplementary Information. In a typical procedure,  $\text{Na}_2\text{HA}$  was mixed with aqueous GO suspension thoroughly under ultrasonic irradiation. Then the mixtures with different GO contents of 50%, 40%, 30%, 20%, 10%, and 5% in weight were dried at  $60^\circ\text{C}$ , and thermally treated at  $200^\circ\text{C}$  for 2 h under an  $\text{Ar}/\text{H}_2$  (5%) atmosphere. 90 mg of pure GO was used for reduction experiments under same conditions, and finally got about 54 mg of rGO. Apparently, the exact weight content of the rGO after treatment should be 3%, 6%, 12%, 18%, 24%, 30%, respectively, based on the weight of the  $\text{Na}_2\text{HA}/\text{GO}$ .

### 2.2. Structural characterization

The morphology of the products was examined by scanning electron microscopy (SEM, FEI, Sirion 200). X-ray photoelectron spectroscopy (XPS) measurements were conducted by a VG MultiLab 2000 system with a monochromatic Al  $K\alpha$  X-ray source (Thermo VG Scientific). Fourier transform infrared spectra were recorded using a VERTE 70 (Bruker Company, Germany) in the wavenumber range from 400 to  $4000\text{ cm}^{-1}$  at room temperature. Liquid Chromatograph Mass

Spectrometer (LC-MS) chromatograms were conducted by a liquid chromatograph mass spectrometer (1100 LC-MSD-Trap-XCT, Agilent).

### 2.3. Electrochemical characterization

The  $\text{Na}_2\text{HA}/\text{rGO}$  (3 wt% rGO, 6 wt% rGO, 12 wt% rGO, 18 wt% rGO, 24 wt% rGO, 30 wt% rGO),  $\text{Na}_2\text{HA}$ , and rGO electrodes were prepared by grinding 60 wt% active materials, 30 wt% super P, and 10 wt% PVDF dissolved in N-methyl-2-pyrrolidone (NMP). Then the slurry was coated onto undefiled Cu foils, dried in an oven at  $80^\circ\text{C}$  for 20 h, and punched into wafers with a diameter of 8 mm. The loading of the active material of  $\text{Na}_2\text{HA}/\text{rGO}$ ,  $\text{Na}_2\text{HA}$  are about  $0.6\text{--}1.0\text{ mg cm}^{-2}$ . The assembled CR2032 half coin cells consist of the corresponding electrode slices, glass fiber membranes (GF/D, Whatman),  $150\text{ }\mu\text{L}$  of 1 M  $\text{NaClO}_4$  dissolved in a mixture of ethylene carbonate (EC) and polypropylene carbonate (PC) (1:1 by volume) or Triethylene glycol dimethyl ether (TEGDME) as the electrolyte, and sodium metal as the counter electrode. The sodium-ion full cell is composed of the pre-sodiation  $\text{Na}_2\text{HA}/\text{rGO}$  electrode [42],  $150\text{ }\mu\text{L}$  of 1 M  $\text{NaClO}_4$  dissolved in a mixture of EC and PC (1:1 by volume) as the electrolyte, and the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  electrode as the cathode. Besides, the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  electrode consists of 70 wt% active materials, 20 wt% super P, and 10 wt% PVDF in NMP. Considering the evaluation on anode materials, the loading of the active material of the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  electrode is  $3\text{ mg cm}^{-2}$  and the diameter of electrode wafers is 12 mm. So the specific capacity of the full battery is calculated according to the quantity of anode materials in this work. Galvanostatic charge–discharge tests were carried out on a Land Battery Measurement System (Land) and the cyclic voltametric (CV) measurements were conducted on an electrochemical workstation (CHI 660D, China). With respect to the electrochemical impedance spectroscopy (EIS) measurement, the open-circuit potential was adopted, and the voltage amplitude was 5 mV. For ex-situ Fourier Transform Infrared (FTIR) Spectroscopy and ex-situ XPS characterizations, the half cells at different charge and discharge states were disassembled by the battery sealing machine, and the whole process was conducted in an Ar-filled glove box with water/oxygen content lower than 1 ppm. Then the relevant electrode slices were rinsed with the solvent of pure propylene carbonate (PC) for several times and dried completely in the Ar-filled glove box for 72 h. Active

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