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## **Facile synthesis of amorphous Cr<sub>2</sub>O<sub>3</sub>/N-doped carbon nanosheets and its excellent lithium storage property**

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**Abstract:** The  $\text{Cr}_2\text{O}_3$  with high energy density and relatively low lithium insertion potential is a promising anode candidate for LIBs. However, the intrinsic poor electroconductivity and side effects like volume expansion of  $\text{Cr}_2\text{O}_3$  severely limit its capacity and cyclability at high charge/discharge rates. To address the problem, the amorphous  $\text{Cr}_2\text{O}_3/\text{N}$ -doped carbon nanosheets (denoted as  $a\text{-Cr}_2\text{O}_3/\text{NC}$ ) have been designed and prepared by an easy one-step solution combustion synthesis method from a uniform solution of chromium nitrate, glucose and glycine. The as-synthesized  $a\text{-Cr}_2\text{O}_3/\text{NC}$  consist of amorphous  $\text{Cr}_2\text{O}_3$  particles and N-doped carbon sheet, where the amorphous  $\text{Cr}_2\text{O}_3$  is evenly encapsulated in the carbon sheet support. An anode prepared from the synthesized  $a\text{-Cr}_2\text{O}_3/\text{NC}$  demonstrates much higher specific capacity and better cycling performance than the crystalline  $\text{Cr}_2\text{O}_3$  anode. Upon extended cycling, the  $a\text{-Cr}_2\text{O}_3/\text{NC}$  anode exhibits good long-term stability and its reversible capacity retains as high as  $782.4 \text{ mAh g}^{-1}$  after 500 cycles at  $1 \text{ A g}^{-1}$ . Such good performance stems from its unique structure. The amorphous structure of  $\text{Cr}_2\text{O}_3$  can furnish a mass of enterable active sites which can favor the lithium ions insertion/extraction, while the sheet-like N-doped carbon support can increase the electroconductivity and facilitate the transportation of lithium ions and electrons.

**Keywords:** Solution combustion synthesis, Amorphous,  $\text{Cr}_2\text{O}_3/\text{C}$  nanosheets, Anode materials.

## 1. Introduction

To solve the problem of energy demands, great efforts have been made to develop renewable energy resources<sup>[1, 2]</sup>. Lithium-ion batteries (LIBs) are in great demand as a sustainable power source for consumer electronics and hybrid electric vehicles<sup>[3]</sup>, with high power density, high voltage and long lifespan<sup>[4-8]</sup>. Currently, graphite as anode material is broadly used in commercial LIBs, but its theoretical maximum capacity is only 372 mAh g<sup>-1</sup><sup>[9, 10]</sup>. With rapidly increasing demands in LIBs market, it is urgent to address the need to replace graphite with new anodes materials that have higher specific capacity. A variety of transition metal oxides (MO<sub>x</sub>, M: Cr, Fe, Ti, etc.) as the anode materials have been explored for LIBs<sup>[11-14]</sup>. Among the transition metal oxides, Cr<sub>2</sub>O<sub>3</sub> has become a promising candidate owing to its high theoretical capacity of 1058 mAh g<sup>-1</sup> and relatively low electromotive force value of 1.085 V<sup>[15, 16]</sup>. However, Cr<sub>2</sub>O<sub>3</sub> has encountered challenges such as fast capacity fading and poor rate performance, due to its poor electroconductivity, large volume expansion and structural destruction during the charge/discharge cycling<sup>[17, 18]</sup>.

In recent years, many strategies have been introduced to overcome the above problems of Cr<sub>2</sub>O<sub>3</sub>, e.g., constructing distinctively porous nanostructures<sup>[19, 20]</sup>, hetero-atom doping<sup>[21]</sup>, and preparing Cr<sub>2</sub>O<sub>3</sub>/carbon composites with suitable microstructure<sup>[22, 23]</sup>. Among these methods, the preparation of Cr<sub>2</sub>O<sub>3</sub>/carbon composite has been widely investigated, in which carbon can not only improve the electroconductivity of active materials and facilitate the transportation of lithium ions and electrons, but also cushion the stress from volume expansion of active materials and prevent the aggregation and pulverization of nanoparticles

[18,22]. Furthermore, as reported in many literatures [24-26], N-doping can improve electrochemical performances of metal oxides/carbon composite. Xu et al. [25] prepared N-doped carbon-coated TiO<sub>2</sub> coaxial nanofibers, which exhibit superior features with a reversible capacity of 284 mAh g<sup>-1</sup> after 100 cycles at 0.1A g<sup>-1</sup>. Moreover, according to some literatures of other metal oxides (MO<sub>x</sub>, M: Fe, V, etc.), it has been proven that the amorphous nature of metal oxides can effectively accommodate stress, during the Li<sup>+</sup> insertion/extraction process, while the defects in amorphous structure can serve as reversible Li<sup>+</sup> storage sites for LIBs, which contributes to the good electrochemical performance [27-29]. Huang et al. [29] reported that when compared with its crystalline counterpart, the amorphous nature of Fe<sub>2</sub>O<sub>3</sub> facilitates interfacial lithium storage of the active materials and enhances capacitive-like lithium storage, leading to much higher reversible capacity and longer cycle stability. Consequently, design and construction of amorphous Cr<sub>2</sub>O<sub>3</sub>/N-doped carbon nanosheets as anodes for LIBs is extremely desirable to achieve both high capacity and long cycling life.

In this work, we firstly report the amorphous Cr<sub>2</sub>O<sub>3</sub>/N-doped carbon nanosheets (denoted as *a*-Cr<sub>2</sub>O<sub>3</sub>/NC) synthesized by a simple and facile, one-step solution combustion synthesis (SCS) method. In the SCS process, chromium nitrate was used as the chromium source and oxidant, while glycine as the fuel and glucose as the carbon source. This synthesis approach involves an instantaneous and self-sustained redox reaction in a homogeneous aqueous solution. It is a time- and energy-efficient process. The released heat can sustain the entire reaction, and the quality of the combustion products can be controlled by adjusting the combustion parameters. Most importantly, all reactants materials with the homogeneous mixing at the molecular level in the solution renders the uniform distribution of the

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compositions of the products<sup>[30-32]</sup>. In the synthesis process, chromium nitrate and glucose are transformed into chromium oxide and carbon, respectively, and amorphous chromium oxide is homogeneously distributed in the carbon sheet support. During the electrochemical measurement, the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC presents superior lithium storage performance with high reversible capacity, long-term stability upon extended cycling (782.4 mAh g<sup>-1</sup> after 500 cycles at 1 A g<sup>-1</sup>) and good rate capability.

## 2. Experimental

### 2.1. Materials synthesis

The raw materials were chromium nitrate (Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 0.025mol, chromium source and oxidant), glycine (C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>, 0.01mol, fuel) and glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, 0.0375mol, carbon source). All reactants were dissolved in 100 mL deionized water in a 500 mL glass beaker to prepare mixture solution. The solution was heated in a temperature-controlled electrical furnace (the peak temperature of 400 °C) in air. The heating rate was controlled at 20 K min<sup>-1</sup>. When heated to around 175 °C, the solution was evaporated to gradually form black gel. Then, the gel swelled and a smoldering combustion reaction occurred, coupled with the release of a great many of gases. The entire process only lasted a few minutes and finally resulted in the formation of a foamy and porous combustion product. The bare Cr<sub>2</sub>O<sub>3</sub> (denoted as *c*-Cr<sub>2</sub>O<sub>3</sub>) for comparison was synthesized in the same process without the addition of glucose.

## 2.2. Materials characterization

The compositions of the products were identified by the X-Ray diffraction (XRD) using Cu K $\alpha$  ( $\lambda=0.1542$  nm) radiation (Rigaku D/max-RB12) at a scanning rate of  $10^\circ \text{ min}^{-1}$ . Thermal gravimetric analysis (TG) was recorded at a heating rate of  $10^\circ \text{ C min}^{-1}$  in air using a Rigaku DT-40 thermal analyzer. X-ray photoelectron spectra (XPS) (ESCALAB 250, PerkinElmer) were used to characterize the surface chemistry. Raman spectra were measured with a laser excitation wavelength of 532 nm (Jobin-Yvon HR300). The morphology was observed by field emission scanning electron microscopy (FE-SEM, ZEISS ULTRA 55). Transmission electron microscopic (TEM) images and energy dispersive X-ray spectra (EDS) were obtained on a transmission electron microscope (JEOL, JEM-2010).

## 2.3. Electrochemical measurements

First, the CR2023-type coin cells were constructed. The as-synthesized products (the active materials), acetylene black (AB, the conducting material) and polyvinylidene fluoride (PVDF, the binder) were mixed in a weight ratio of 80:10:10 to prepare the electrode (working electrode). The mixture was blended with the N-methylpyrrolidone solvent to form slurry. The slurry was evenly coated on the Cu foil with a blade and was dried at  $120^\circ \text{ C}$  in a vacuum oven for 12 h, and then pressed at 10 MPa. The mass loading of the active materials was  $\sim 2 \text{ mg cm}^{-2}$  in the obtained electrodes. The cells of CR2032-type coin were assembled in a glove box for electrochemical measurement. 1 M LiPF $_6$  in a dimethyl carbonate (DMC): ethylene carbonate (EC) (1:1 by volume) was used as electrolyte, while Li foil as the counter. This article is protected by copyright. All rights reserved.

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electrode. Galvanostatic charge/discharge tests were performed in the potential window of 0.01-3 V at 25 °C using a LAND CT-2001A. Cyclic voltammetry (CV) curves were collected at 0.5 mV s<sup>-1</sup> in the 0.01-3.0 V range using an electrochemistry workstation (CHI618D). Electrochemical impedance spectroscopy (EIS) data were obtained over a frequency range of 10 mHz to 100 kHz using the same instrument.

### 3. Results and discussion

XRD patterns of the synthesized *a*-Cr<sub>2</sub>O<sub>3</sub>/NC and *c*-Cr<sub>2</sub>O<sub>3</sub> are showed in Fig. 1. The *c*-Cr<sub>2</sub>O<sub>3</sub> without the addition of glucose exhibits the obvious Bragg diffraction peaks, which are indexed to the crystalline Cr<sub>2</sub>O<sub>3</sub> phase (the lattice parameters: a=b=0.4959nm, c=1.3594 nm; JCPDS #38-1479). However, the XRD profile of the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC composite shows no obvious Bragg diffraction peaks, indicating that the product is amorphous. During SCS, the energy generated by the chemical reaction depends on the ratio of fuel to metal nitrates and usually governs state of the products<sup>[30, 31]</sup>. For the XRD result, it is ascribed that the dehydration and carbonization reaction of glucose needs to absorb energy, leading to that the energy evolved from the combustion process is insufficient to facilitate the crystallization of the products.

The XPS spectra of the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC are presented in Fig. 2. In Fig. 2a, the XPS survey scan illustrates the presence of Cr, C, N and O elements in the prepared composite samples. Fig. 2b reveals the high-resolution spectrum of Cr 2p. The Cr 2p spectrum displays the existence of the doublet Cr 2p<sub>3/2</sub> and Cr 2p<sub>1/2</sub> with binding energies of 576.9 eV and 586.4 eV. This article is protected by copyright. All rights reserved.

eV, respectively <sup>[33]</sup>. In Fig. 2c, the C 1s spectrum peak at 284.7 eV is attributed to the C-C bond with sp<sup>2</sup> orbital. The two peaks located at 286.3 eV and 288.6 eV, which correspond to the oxygen bound species C-O and C=O, respectively <sup>[34, 35]</sup>. The N 1s XPS spectrum of product is presented in Fig. 2d. The peaks around 398 eV and 400 eV illustrate the existence of -N= (398.0 eV) and -NH- (400.2 eV) <sup>[25, 26]</sup>, indicating that N-doping carbon composites are obtained in the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC.

To estimate the carbon content in the obtained *a*-Cr<sub>2</sub>O<sub>3</sub>/NC, the TG test was performed. In Fig. 3a, it can be noticed that up to 200 °C, the weight loss of 5 % is ascribed to the residual moisture evaporation on the surface of *a*-Cr<sub>2</sub>O<sub>3</sub>/NC. A significant weight loss of 22% is observed at temperatures from 200 to 375 °C, after which a gradual loss of ~10% occurs until 900 °C. It is believed that carbon oxidation to CO and CO<sub>2</sub> contributes primarily to the weight loss. The original weight fraction of carbon in the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC is estimated to be 32wt. %. Fig. 3b displays the Raman spectra of the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC. Two broad peaks related to the disordered carbon (D band, 1352 cm<sup>-1</sup>) and graphitized carbon (G band, 1594 cm<sup>-1</sup>) are observed. The intensity ratio (I<sub>D</sub>/I<sub>G</sub>) of the two peaks is 1.4 by fitting the D and G band, indicating the low graphitization degree <sup>[18, 25]</sup>. The result further confirms the amorphous state of the carbon in the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC.

Fig. 4a and d show typical FESEM images of the *c*-Cr<sub>2</sub>O<sub>3</sub> samples and the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC, respectively. It is obvious that the two products present a two-dimensional (2D) sheet structure. To acquire more information about the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC and the *c*-Cr<sub>2</sub>O<sub>3</sub> samples, the TEM analysis was performed. In Fig. 4b, the *c*-Cr<sub>2</sub>O<sub>3</sub> samples consist of nanoparticles, which

present a typical polycrystalline  $\text{Cr}_2\text{O}_3$  phase in the selected area electron diffraction (SAED). In Fig. 4c, from the high-resolution TEM (HRTEM) image, the planar distance of the  $c\text{-Cr}_2\text{O}_3$  samples is approximately 0.2665nm, corresponding to the (104) plane of  $\text{Cr}_2\text{O}_3$ . This further confirms the nanoparticles to be the  $\text{Cr}_2\text{O}_3$ . However, the TEM image clearly displays the sheet-like morphology of the  $a\text{-Cr}_2\text{O}_3/\text{NC}$  composite in Fig. 4e, which concurs with the FESEM image. No diffraction rings are observed in SAED and the HRTEM (Fig. 4f) image does not show any crystalline lattice fringes, further confirming the amorphous structure of the  $a\text{-Cr}_2\text{O}_3/\text{NC}$ . This is in accord with the XRD results. EDS elemental mapping results (Fig. 4g, h, i, j) clearly reveal that the elements Cr, O and C are homogeneously distributed throughout the sample, indicating that the  $\text{Cr}_2\text{O}_3$  particles are uniformly encapsulated in the carbon sheet support.

The electrochemical performance of the  $a\text{-Cr}_2\text{O}_3/\text{NC}$  was investigated in a half-cell setup. The CV curves of the  $a\text{-Cr}_2\text{O}_3/\text{NC}$  are shown in Fig. 5a for the initial four cycles in the 0.01-3.0 V range vs.  $\text{Li}/\text{Li}^+$  at a scan rate of  $0.5 \text{ mV s}^{-1}$ . The cathodic peak at 0.70 V is ascribed to decomposition of the electrolyte and concomitant formation of solid electrolyte interphase (SEI) <sup>[22, 36]</sup>, which disappears in the subsequent cycles. The peak around 0.01 V relates with the reaction of  $\text{Cr}_2\text{O}_3$  with  $\text{Li}^+$  <sup>[37, 38]</sup>. In the anodic scan, two peaks at about 1.08 V and 0.2 V are observed, corresponding to the reversible oxidation of  $\text{Cr}^0$  to  $\text{Cr}^{3+}$  and the decomposition of  $\text{Li}_2\text{O}$ , respectively <sup>[38, 39]</sup>. In the following cycles, the integrated peak area on the CV curves does not change, indicating good charging and discharging reversibility of the  $a\text{-Cr}_2\text{O}_3/\text{NC}$  anode.

The charge/discharge curves of the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC composite at a current density of 1 A g<sup>-1</sup> between 0.01 V and 3.0 V (vs. Li/Li<sup>+</sup>) are shown in Fig.5b. For the first discharge, the discharge capacity of the electrode is as high as 1307 mAh g<sup>-1</sup>, much higher than the theoretical value (1058 mAh g<sup>-1</sup>), which can be ascribed to the irreversible reductive electrolyte decomposition and the SEI layer formation for most metal oxide anode materials [40-43]. For the following cycles, the discharge capacity decreases and stabilizes. The corresponding plateaus are shown on the charge curves, which is relevant to the Li<sup>+</sup> ion de-intercalation. The plateaus on the charge and discharge curves are all observed upon cycling, indicating the reversible insertion/extraction reactions.

Fig. 5c presents the cycling performance at 1 A g<sup>-1</sup> in the voltage range of 0.01 to 3 V versus Li<sup>+</sup>/Li of the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC anode and the *c*-Cr<sub>2</sub>O<sub>3</sub> anode. The *a*-Cr<sub>2</sub>O<sub>3</sub>/NC electrode displays much better cyclic stability and capacity retention than that of *c*-Cr<sub>2</sub>O<sub>3</sub>. During the first 20 cycles of the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC, the reversible capacity continuously decreases, a common phenomenon for many transition metal oxide anodes [44-46]. In subsequent cycles, the reversible capacity gradually increases to 653 mAh g<sup>-1</sup> at the 100th cycle, indicating a re-activation process, which might be ascribed to stable SEI optimization and refinement in anode structure [47, 48]. Then the capacity remains stable at approximately 653 mAh g<sup>-1</sup> with a coulombic efficiency of 99.3% in the 100th cycle. In contrast, the storage capacity of the *c*-Cr<sub>2</sub>O<sub>3</sub> gradually declines and finally stays at approximately 144.9 mAh g<sup>-1</sup> over 100 cycles.

The rate performance of the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC anode and the *c*-Cr<sub>2</sub>O<sub>3</sub> anode were tested at different current densities. As observed in Fig. 5d, the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC anode delivers better

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reversible capacity of 790.4 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup>, 534.6 mAh g<sup>-1</sup> at 0.2 A g<sup>-1</sup>, 373.8 mAh g<sup>-1</sup> at 0.5 A g<sup>-1</sup>, 315.3 mAh g<sup>-1</sup> at 1 A g<sup>-1</sup>, 282.9 mAh g<sup>-1</sup> at 2A g<sup>-1</sup>, 250.1 mAh g<sup>-1</sup> at 5 A g<sup>-1</sup>, 233.4 mAh g<sup>-1</sup> at 10 A g<sup>-1</sup>, respectively. Notably, as the current density returned to 0.1 A g<sup>-1</sup>, a high reversible capacity of 743.6 mAh g<sup>-1</sup> was obtained, after the rate performance test. Obviously, the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC anode exhibits better the rate capabilities than the *c*-Cr<sub>2</sub>O<sub>3</sub> anode. It can be attributed to the microstructure of the well-distributed amorphous Cr<sub>2</sub>O<sub>3</sub> in the N-doped carbon support, which shortens the transmission distance of electrons and ions, cushions the Cr<sub>2</sub>O<sub>3</sub> volume expansion and furnishes more electrode/electrolyte interface area.

The cycling stability of the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC anode is further investigated at a current density of 1 A g<sup>-1</sup> up to 500 cycles. In Fig. 5e, the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC electrode exhibits a relatively stable capacity for more than 500 cycles. The capacity in the 500th cycle is still as high as 782.4 mAh g<sup>-1</sup>. In addition, the Coulombic efficiency is close to 100% over the 500 cycles. This indicates that the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC anode for LIBs shows good cycle stability and long cycle life at high current densities.

The EIS measurements are presented in Fig. 6. Both composite and monolithic anodes show a typical semicircle and inclined lines in Nyquist plots (an equivalent circuit is also shown in Fig. 6). It is reported that the semicircle diameter is relevant to the charge-transfer resistance (R<sub>ct</sub>) at the electrode/electrolyte interface and the lithium ions migration resistance (R<sub>sf</sub>) via the SEI film<sup>[29, 49, 50]</sup>. The inclined line in the lower frequency region indicates the Warburg impedance (Z<sub>w</sub>), corresponding to the diffusion of lithium ions into the bulk of the electrodes<sup>[22, 51]</sup>. As seen in Fig. 5, the semicircle diameter in the high-to-medium frequency

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region for the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC electrode is smaller than that of the *c*-Cr<sub>2</sub>O<sub>3</sub>, indicating a lower value of R<sub>sf</sub> and R<sub>ct</sub> for the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC composite anode. In the low frequency region, the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC shows a steeper slope than the *c*-Cr<sub>2</sub>O<sub>3</sub>, indicating a lower value of Z<sub>w</sub> and better lithium ions diffusion mobility. In addition, the steeper line is also considered to improve capacitive-like behavior of electrode <sup>[29]</sup>. Overall, these results suggest that the intimately combined the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC with the N-doped carbon support and amorphous Cr<sub>2</sub>O<sub>3</sub> improves electrical conductivity and shortens the transmission distance of lithium ions and electrons, resulting in fast charge/discharge rates.

In comparison with the other Cr<sub>2</sub>O<sub>3</sub>-based anode, the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC anode also shows better Li-ion storage capacity at high current densities (Table 1). It is believed that the N-doped carbon sheet increases the electrical conductivity and the amorphous structure mitigates lattice stress and provides open vacancies, voids and defects for the diffusion of faster Li<sup>+</sup>. Clearly, the amorphization of Cr<sub>2</sub>O<sub>3</sub> and the sheet-like N-doped carbon support both effectively increase the capacity of lithium-storage. In addition, the open structure in the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC anode help to accommodate the volumetric change in the electrode during cycling, thus ensuring the electrode stability <sup>[29]</sup>. All these factors contribute to the outstanding electrochemical properties of the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC anode.

## Conclusions

In summary, the amorphous  $\text{Cr}_2\text{O}_3/\text{N}$ -doped carbon nanosheets were successfully prepared first-ever, by a facile solution combustion synthesis method. The obtained  $a\text{-Cr}_2\text{O}_3/\text{NC}$  are composed of amorphous  $\text{Cr}_2\text{O}_3$  and N-doped carbon sheets, where the amorphous  $\text{Cr}_2\text{O}_3$  is homogeneously embedded. The  $a\text{-Cr}_2\text{O}_3/\text{NC}$  anode shows a much higher capacity and more stable cycling performance at  $1 \text{ A g}^{-1}$  as compared to the  $c\text{-Cr}_2\text{O}_3$  anode. The unique sheet-like N-doped carbon support increases the electroconductivity, cushions the  $\text{Cr}_2\text{O}_3$  volume expansion and facilitates the carriage of lithium ions and electrons. Meanwhile, the amorphous  $\text{Cr}_2\text{O}_3$  mitigates lattice stress and provides open vacancies, voids and defects to accommodate faster  $\text{Li}^+$  insertion/extraction. This work introduces an attractive route to design and construct the amorphous transition metal oxides/carbon nanosheets as anode materials for high-performance LIBs.

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### Captions to Figures:

Fig.1. XRD patterns of the synthesized the  $a\text{-Cr}_2\text{O}_3/\text{NC}$  and  $c\text{-Cr}_2\text{O}_3$ .

Fig.2. The XPS spectra of the  $a\text{-Cr}_2\text{O}_3/\text{NC}$ : survey scan (a) and high resolution spectra of (b) Cr 2p, (c) C 1s, and (d) N 1s.

Fig.3. (a) TG curve of the  $a\text{-Cr}_2\text{O}_3/\text{NC}$  under an air atmosphere. (b) Raman spectra of the  $a\text{-Cr}_2\text{O}_3/\text{NC}$  in the range of  $800\text{-}2000\text{ cm}^{-1}$ .

Fig. 4. FESEM images of (a)  $c\text{-Cr}_2\text{O}_3$  and (d)  $a\text{-Cr}_2\text{O}_3/\text{NC}$ ; TEM image of (b)  $c\text{-Cr}_2\text{O}_3$  and (e) the  $a\text{-Cr}_2\text{O}_3/\text{NC}$  (inset: the electron diffraction pattern); The high resolution TEM of (c)

*c*-Cr<sub>2</sub>O<sub>3</sub> and (f) *a*-Cr<sub>2</sub>O<sub>3</sub>/NC; (g) TEM image and (h, i, j) The element distribution images (Cr, O, C) of the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC.

Fig. 5. (a) CV curves for the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC at a scan rate of 0.5 mV s<sup>-1</sup> in the range of 0.01 to 3.0 V versus Li/Li<sup>+</sup>; (b) The first four charge/discharge curves of the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC at a current density of 1A g<sup>-1</sup>; (c) Comparison of cycling performance of *a*-Cr<sub>2</sub>O<sub>3</sub>/NC and *c*-Cr<sub>2</sub>O<sub>3</sub> at the current density of 1A g<sup>-1</sup>; (d) rate capabilities of the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC and *c*-Cr<sub>2</sub>O<sub>3</sub>; (e) Subsequent cycling of *a*-Cr<sub>2</sub>O<sub>3</sub>/NC at a current density of 1A g<sup>-1</sup>.

Fig. 6. Nyquist plots of the *a*-Cr<sub>2</sub>O<sub>3</sub>/NC and *c*-Cr<sub>2</sub>O<sub>3</sub> at fresh coin cells over the frequency range from 100 kHz to 0.01 Hz.

## Captions to Table:

Table 1. Electrochemical performance of the  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>/NC anode material compared with other chromium oxide anode materials in previous works.

**Table 1**

The structure of material	Specific discharge capacity (mAh g <sup>-1</sup> )	Rate capability (mAh g <sup>-1</sup> )	References
Cr <sub>2</sub> O <sub>3</sub> -C hierarchical core/shell nanospheres	600 after 35 cycles at 211.6 mA g <sup>-1</sup>	-	18
Highly ordered mesoporous Cr <sub>2</sub> O <sub>3</sub>	521 after 100 cycles at 105.8 mA g <sup>-1</sup>	-	19
Cr <sub>2</sub> O <sub>3</sub> /FLG/Ni	~692.2 after 100 cycles at 50 mA g <sup>-1</sup>	534.2 (200 mA g <sup>-1</sup> ) 378.8 (400 mA g <sup>-1</sup> ) ~570 (211.6 mA g <sup>-1</sup> )	21
Carbon-coated graphene-Cr <sub>2</sub> O <sub>3</sub> composites	~550 after 100 cycles at 105.8 mA g <sup>-1</sup>	~380 (529 mA g <sup>-1</sup> ) ~290 (1058 mA g <sup>-1</sup> )	22
Cr <sub>2</sub> O <sub>3</sub> /C nanocomposites	465.5 after 150 cycles at 100 mA g <sup>-1</sup>	448.7 (200 mA g <sup>-1</sup> ) 287.2 (400 mA g <sup>-1</sup> ) 144.8 (800 mA g <sup>-1</sup> )	25
Mesoporous carbon-Cr <sub>2</sub> O <sub>3</sub> composite	639 after 80 cycles at 50 mA g <sup>-1</sup>	- ~280 (1.058 A g <sup>-1</sup> )	36
Mesoporous Cr <sub>2</sub> O <sub>3</sub> sheet	480 after 55 cycles at 105.8 mA g <sup>-1</sup>	~190 (2.116 A g <sup>-1</sup> ) ~110 (10.58 A g <sup>-1</sup> )	37
Sandwich-like Cr <sub>2</sub> O <sub>3</sub> -graphite intercalation composites	480 after 1000 cycles at 100 mA g <sup>-1</sup>	- 315.3 (1 A g <sup>-1</sup> )	43
A-Cr <sub>2</sub> O <sub>3</sub> /NC	728.4 after 500 cycles at 1000 mA g <sup>-1</sup>	282.9 (2 A g <sup>-1</sup> ) 233.4(10 A g <sup>-1</sup> )	Our work









