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α -Fe₂O₃ anchored on porous N doped carbon derived from green microalgae *via* spray pyrolysis as anode materials for lithium ion batteries



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ABSTRACT

The α -Fe₂O₃@nitrogen doped carbon (as donated α -Fe₂O₃@NC) composites derived from green microalgae was synthesized using one-pot spray pyrolysis, which showed a high discharge capacity of 1281.5 mAh g⁻¹ at 100 mA g⁻¹ as anode materials for lithium ion storage. They also provided good rate performance in a range of 200 mA g⁻¹–1000 mA g⁻¹, and maintained a capacity of 92% after 100 cycles at 200 mA g⁻¹. It demonstrated not only improved electrical conductivity but also effective prevention of the volume expansion of iron oxide during battery charge/discharge by uniformly forming iron oxide nanoparticles on microalgae *via* spray pyrolysis.

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Introduction

As the market for electric vehicles and renewable energy is expanding due to the increase of greenhouse gas emissions and shortage of energy, lithium ion batteries (LIBs) with high storage capacity and cycling stability are desired as a promising power source [1–4]. Accordingly, development of an electrode material, possessing a high energy and power densities with a low cost, is necessary for a future secondary battery system [5].

Graphite has been continuously used as an anode material for commercial LIBs because of its decent electrical conductivity and stable structure preservation under electrochemical reactions. However, graphite has a relatively low theoretical capacity (372 mAh g^{-1}) , which is insufficient to meet an ever increasing energy demands for future [6,7].

Unlike the intercalation based graphite anode, conversion type transition metal oxides (TMOs), $MO_x + 2xLi \leftrightarrow M + xLi_2O$ where M is a transition metal (M = Mn, Fe, Co, Sn), has much higher capacity (*e.g.*

700–1000 mAh g^{-1}) than that of graphite [6–13]. Among a typical TMO, iron oxide has been regarded as a promising anode material due to its earth abundance, high corrosion resistance, environmental friendliness, and high theoretical capacity ($Fe_2O_3 = 1005 \text{ mAh}$ g^{-1} , Fe₃O₄ = 930 mAh g^{-1})[13–17]. However, the volume fluctuation of iron oxide under lithiation/delithiation leads to agglomeration of the active material, electrode pulverization, and loss of electrical connectivity, which ultimately decrease capacity retention rates [18,19]. Also, when a thick and unstable solid electrolyte interphase (SEI) film is formed at iron oxide interface, large amount of lithium is consumed, and a large irreversible capacity is obtained. Hence, many researchers have made great efforts to solve above problems [20], and one of an effective solution to these obstacles is to synthesize nanoscale particles that mitigate the diffusion path of lithium ions [15,21]. An another approach is to construct nanocomposites with carbonaceous matrix that acts as a volumetric buffer and a conductive network to alleviate internal stress and enhance Li ion diffusion by preventing accumulation of SEI [15,16]. Also, utilizing micro/nano-porous materials can improve active material utilization and accommodate volume changes [17,22]. Based on the above reasons, the preparation of nano-sized Fe₂O₃ covered by the conductive carbon matrix, which have micro or nano porous structure is the one of effective approaches to derive highperformance for lithium anode materials.

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Recently, biotemplates, which has unique structures and rich carbon sources, attracted attentions due to their low cost, facile synthesis, reproducibility and environmental benefits. Many biomaterials (such as microalgae, Bamboo, Bacterial Cellulose, etc.) have been often used to create hierarchical nanostructured structures that exhibit excellent electrochemical performance for LIBs [23–30]. Compared with other artificial/biological molds, the green microalgae, natural biological material of spherical microalgae with an average diameter of 0.4 μ m, is used in this study and has the following characteristics.

First, green microalgae can be used as an environmentally friendly energy source. Green microalgae are produced by increasing nutrients such as nitrogen and phosphorus in aquatic ecosystems of rivers, seas, and lakes. Not only it consumes dissolved oxygen of lake but also bad smell and toxic substances damage other organisms and pollute water. The use of green microalgae has the strong point that it can be used as the anode material for LIBs with mitigation of harmful substances [31,32]. Second, as the cell wall of green microalgae is composed mainly of polysaccharides, green microalgae cells can adsorb metal ions through electrostatic interactions, which is suitable for deriving TMOs [23,33,34]. Third, carbon matrix can be derived from the cells due to the richness of carbohydrates [23,28]. Thus, deriving α -carbon coated iron oxide (Fe₂O₃) provides both environmental and technical benefits.

In this work, a new synthesis strategy combining biotemplate method and spray pyrolysis is proposed to prepare α -Fe₂O₃ anchored on porous nitrogen doped carbon (namely, α -Fe₂O₃@NC). Furthermore, the properties of α -Fe₂O₃@NC are investigated by XRD, SEM, TEM and XPS. The electrochemical properties of α -Fe₂O₃@NC and bare α -Fe₂O₃ are examined from cyclic voltammetry (CV), galvanostatic cyling, and AC impedance spectroscopy (EIS).

Experimental

The main preparation processes are shown in Fig. 1. This new strategy will provide great alternatives for the usage of green microalgae and extend the range of biotemplating and spray pyrolysis to derive electrochemically functional materials for batteries. As illustrated in Fig. 2, the green microalgae, *Nephroselmis* sp. KGE8, for this study were supplied by KIST Green city Technology Institute. Green microalgae were used after washing and centrifuging to remove impurities. The spray solution was prepared by dissolving the green microalgae grown in 0.3 M iron nitrates in 400 mL distilled water and after each 1 h biosorption.

The α -Fe₂O₃@NC composites powder was prepared from spray solution by one-pot ultrasonic spray pyrolysis. A quartz reactor with a length of 1000 mm and a diameter of 55 mm was used. The temperature was maintained at 800 °C, and the flow rate of the nitrogen carrier gas was set to 10 L min⁻¹. The α -Fe₂O₃ bare powder was synthesized under the same conditions using 0.3 M iron nitrate.

The crystal structure of the powders was characterized by X-ray diffraction analysis (XRD, Rigaku DMAX-33) using Cu Kα radiation at room temperature in the 2θ range of $10-80^{\circ}$. The morphological characteristics of these powders were investigated using field emission scanning electron microscopy (NOVA NanoSEM200) and high resolution transmission electron microscope (TEM, FEI, Talos). The Brunauer-Emmett-Teller (BET) surfaces area of the powder was measured using a Micromeritics ASAP 2020 Porosimeter test station and N₂ gas was used as adsorbents. The sample was degassed in a vacuum 300°C for 4 h before testing. The specific surface area was calculated from the nitrogen adsorption data using the BET method at a relative pressure range (P/P_0) of 0.05– 0.20. The porosity distribution was calculated from the adsorption branch using the BJH (Barrett-Joyner-Halenda) equation. X-ray photoelectron spectroscopy (XPS) spectra of the powders were obtained using PHI 5000 VersaProbe (Ulvac-PHI) with Al Ka radiation (1486.6 eV). To determine the amount of carbon in the powder, thermogravimetric analysis (TGA, TA korea/SDT Q600) was performed at a heating rate of 10 °C min⁻¹ in air.

The capacity and cycle characteristics of the powders were measured by a 2032 coin cell model. The electrode was prepared by mixing 70 wt% active powder, 20 wt% carbon black and 10 wt% carboxymethyl cellulose (CMC) in distilled water. Lithium metal and glass microfiber filter was used as the counter electrode and separator, respectively. 1 M LiPF6 dissolved in a mixture of ethylene carbonate/diethyl carbonate (EC/DEC) at a volume ratio of 1:1 was used as an electrolyte. The above battery assembling process was assembled in a glove box of Ar atmosphere. The charge and discharge characteristics of the coin cell were measured by cycling at potential ranges of 0.01–3.0 V at various current densities. Cyclic voltammetry measurements were performed at a scan rate of 0.1 mV s⁻¹ in the 0.01–3 V range. Electrochemical impedance spectroscopy (EIS) data onto the electrodes were tested and analyzed at room temperature in the frequency range between 0.01 Hz and 100 kHz.

Results and discussion

Fig. 3 shows the XRD patterns of bare α -Fe₂O₃ and α -Fe₂O₃@NC prepared by spray pyrolysis at 800 °C. According to a previous



Fig. 1. Schematic illustration showing the synthesis of α-Fe₂O₃@NC composite via spray pyrolysis.



H 0.01



Fig. 2. (a) Phylogenetic tree showing the relationships among 28S D1–D2 rRNA sequences of isolate *Micractinium reisseri* KGE33 and the most similar sequences retrieved from the National Center for Biotechnology Information (NCBI) nucleotide database. (b) Microscopic images of the microalgae isolate.



Fig. 3. X-ray patterns of the α -Fe₂O₃@NC composite and bare α -Fe₂O₃ powders.

report, this pattern suggests that the pure crystal structure of the α -Fe₂O₃ phase (JCPDS NO. 33-0064) [17]. No additional peaks were observed, and the sharp diffraction peaks demonstrate crystallinity of α -Fe₂O₃ [15]. In addition, the diffraction peaks of α -Fe₂O₃@NC is appeared at 24.1, 33.2, 35.6, 40.9, 49.5, 54.1, 62.4 and 36.4° corresponded to the (012), (104), (110), (113), (024), (116), (214) and (300) planes of α -Fe₂O₃ (JCPDS NO. 33-0064). It means that Iron nitrate and microalgae as precursor were perfectly decomposed and oxidized in short reaction time (<5 s) of spray pyrolysis process. Compared with XRD pattern of bare α -Fe₂O₃, the smaller intensity of peaks for α -Fe₂O₃@NC indicates that carbon matrix from microalgae induce the smaller crystal size and highly distribution of Fe₂O₃ nanoparticles on the carbon materials.

SEM image in Fig. 4a and b shows the morphology of the α -Fe₂O₃@NC composites powder that is in a spherical shape with an



Fig. 4. SEM images of the (a), (b) bare microalgae and (c), (d) α-Fe₂O₃@NC composites.

average particle size of 400 nm. The α -Fe₂O₃@NC (in Fig. 4c and d) show that microsphere is a well-dispersed with particle sizes ranging from 200 to 500 nm. The TEM image (Fig. 5a and b) shows a porous α -Fe₂O₃@NC composites with voids. The high-resolution TEM image (Fig. 5c) of the α -Fe₂O₃@NC composites powder is

clearly represented by the lattice fringes separated by 0.37 nm, which corresponds to the [012] plane of α -Fe₂O₃ [15,35]. The elemental mapping (Fig. 5d) shows that the distribution of Fe, C, and N heteroatoms is well distributed for the micro algae structure, and C and N are derived from green microalgae. The elemental



Fig. 5. Morphologies of the α-Fe₂O₃@NC. (a, b) TEM images, (c) HRTEM images, (d) elemental-mappings of C, Fe, O, and N components.

mapping images of Fe and O implies that the α -Fe₂O₃ nanocrystals are uniformly distributed on the surface of the microalgae.

XPS analysis was performed to confirm the binding states of α -Fe₂O₃@NC as shown in Fig. 6. XPS measurement of the wide-scan spectrum indicate the presence of Fe, O and C, N in the α -Fe₂O₃@NC composites (Fig. 6a). Fig. 6b shows XPS spectrum of the Fe 2p. Two peaks of 710.6 eV and 724.0 eV are assigned to Fe 2p_{3/2} and Fe 2p_{1/2}, indicating the oxidation state of α -Fe₂O₃. In addition, the appearance of satellite peaks at about 719.0 eV (indicated by arrows) confirms the presence of α -Fe₂O₃ in the composites [36,37]. Furthermore, Fig. 6c shows that four distinct peaks were observed at 284.6, 285.9, 286.8, and 288.1 eV, corresponding to the sp² hybridized C—C, C—N, C—O, and C=O groups in the C 1s spectrum, respectively, and these peaks indicated the microalgae

had been carbonized during spray pyrolysis process [8,40]. Despite not using any nitrogen sources (*e.g.* ammonia gas, urea, ethylenediamine, dopamine), these XPS analysis indicated that the presence of nitrogen doped and the evolution of strong interaction between carbon and nitrogen in α -Fe₂O₃@NC. Furthermore, nitrogen has favorable properties for lithium storage, *e.g.* its higher electronegativity than carbon and hybridization of the π electrons with lone pair of nitrogen. It appears to be beneficial for Li facilitation due to the strong interaction between the carbon coating and lithium [38,39]. In Fig. 6d, the N 1s peak has three components, indicating that the N atom is in three different binding properties inserted in the green microalgae network. The peaks located at 398.28, 399.98 and 400.93 eV of the N 1s spectrum indicate the presence of nitrogen atoms structurally incorporated



Fig. 6. (a) XPS survey scan spectra of the samples, narrow scan of (b) Fe 2p, (c) N 1s, (d) C 1s. (e) Schematic illustration of the structure of nitrogen in N-doped carbon materials.

in the carbon matrix as highly active pyridinic (N-6), pyrrolic (N-5) and quaternary (N-Q) nitrogen species [38,40]. In Fig. 6e, among the three nitrogen structures, quaternary nitrogen and pyridinic nitrogen are sp² hybridized and improve the electrochemical performance of the carbon [41–43]. In particular, pyridinic nitrogen provides a low energy barrier to lithium penetration, because it is located at the edge or defect of the carbon layer. Pyridinic nitrogen increase number of defects that help lithium insertions, improving the capacity and transport of Li⁺ [44]. Pyridinic nitrogen (52.21%), pyrrolic nitrogen (32.50%) and quaternary nitrogen (15.28%) are obtained.

The α -Fe₂O₃@NC composites were performed by TGA to determine the weight ratio (weight 8.3%) of α -Fe₂O₃ and green microalgae (Fig. 7a). The TG curves performed in the air atmosphere shows a small weight loss below 100 °C as adsorbed water at the surface evaporate [24]. A distinct weight loss occurs at 200-500 °C, and carbon content of the composites are 8.3%. The N₂ adsorption-desorption isotherm and pore size distribution of the α -Fe₂O₃@NC composites powder was shown in Fig. 7b. To examine porous structure of as-prepared α -Fe₂O₃@NC materials, N₂ isotherm at 77 K from BET technique was used. The N2 adsorption--desorption typically shows a Type IV isotherm for mesopores and a clear hysteresis represents the intermediate pores [38], and it is postulated that this pores may be originated from the reaction of some organic or ions in microalgae (e.g. S⁻, Na⁺, Cl⁻, Ca²⁺). The overall porous structure (mesoporous green microalgae) is useful for promoting electrochemical reactions and raising the active material utilization [17]. And it alleviates the volumetric change during the Li⁺ insertion/de-insertion, leading enhanced cycling performance. As a result, a good lithium ion storage performance is expected.

In order to evaluate the electrochemical characteristics of bare α -Fe₂O₃ and α -Fe₂O₃@NC composites, Cyclic voltammograms (CV) of α -Fe₂O₃ and α -Fe₂O₃@NC measured at scan rate of 0.1 mV s⁻¹ over 5 cycles within a voltage window of 0.001–3 V (See Fig. 8a and b). Significant differences are found between the first and subsequent cycles [22]. During the discharge of the first cycle, a strong reduction peak appears at 0.43 V and 0.51 V, corresponding to a reduction reaction in which Li⁺ ions are implanted into α -Fe₂O₃ and metallic Fe and Li₂O are formed, which disappears in subsequent cycles. In the anodic scan, a broad peak appears between 1.6 and 1.9 V, indicating that Fe⁰ is oxidized to Fe²⁺ and Fe³ + [17,21]. In the 2nd–5th cycles (Fig. 8b), anodic lithium extraction is observed at 1.68 and 1.9 V, and cathodic lithium insertion appears at generally 0.87 and 0.80 V. Both are reversible

electrochemical reduction/oxidation reactions [21]. Electrochemical reaction scans are represented by three lithium insertion/deinsertion processes: [22]

$$\alpha - Fe_2O_3 + xLi^+ + xe^- \rightarrow \alpha - Li_xFe_2O_3 \tag{1}$$

$$\alpha - Li_x Fe_2O_3 + (2 - x)Li^+ + (2 - x)e^- \rightarrow Li_x Fe_2O_3$$
(2)

$$Li_{x}Fe_{2}O_{3} + 4Li^{+} + 4e^{-} \leftrightarrow 2Fe^{\circ} + 3Li_{2}O$$
(3)

Fig. 8c and d shows constant current discharge/charge and cycling performance was performed in the voltage range of 0.01-3.0 V. Charge and discharge profiles of bare α -Fe₂O₃ and α -Fe₂O₃@NC composites powder was shown in Fig. 8c. The initial discharge capacities of bare α -Fe₂O₃ and α -Fe₂O₃@NC composites powder was 1004.1 and 1281.5 mAh g⁻¹, respectively. During the discharge process of two samples, a voltage plateau about 0.8 V versus Li/Li⁺ was observed, indicating typical characteristics of the α -Fe₂O₃ voltage trend [21]. In the first cycle of α -Fe₂O₃@NC, irreversible capacity loss (ICL) is observed, which corresponds to ${\sim}27\%$ (346.9 mAh g $^{-1}$). This is common in conversion types anodes such as α -Fe₂O₃, and the extra Li is consumed to form SEI at the carbon and iron oxide [45]. Bare α -Fe₂O₃ showed 48.2% (484.5 mAh g^{-1}) of severe irreversible capacity loss. The Fig. 8(c) shows a welloverlapped charge and discharge curves compare to bare α -Fe₂O₃ for the 2nd–5th cycles of α -Fe₂O₃@NC at a current density of 200 mAh g⁻¹, indicating good reversible reaction and outstanding cycling ability

The Fig. 8d shows the performance of α -Fe₂O₃@NC and bare α -Fe₂O₃ electrodes in the range of increasing current density from 200 to 1000 mA g^{-1} . Compared with bare α -Fe₂O₃, the composites showed much improved rate performance. The composites retained 843.6 mAh g^{-1} at 1000 mA g^{-1} without a significant decrease in capacity after 10 cycles. This excellent capacity is about 3.6 times as high as that of the bare α -Fe₂O₃ with 231.9 mAh g⁻¹. Particularly, when the current density reverted back to 200 mAg^{-1} , a high capacity of $954.9 \text{ mAh} \text{ g}^{-1}$ quickly recovered. The α -Fe₂O₃@NC composites slightly increased at a relatively low current density of 400 mAh g^{-1} and 600 mAh g^{-1} . This may be due to the increased lithium ion accessibility of the hybrid structure during the cycling [22,46]. The long-term cycling performance (discharge capacity) of α -Fe₂O₃@NC and α -Fe₂O₃ composites at current density of 1000 mA g^{-1} is shown in Fig. 8e. Stable performance was observed up to 100 cycles, and the



Fig. 7. (a) TGA of α-Fe₂O₃@NC composite (b) pore-size distributions and the N₂ adsorption-desorption isotherms (inset) of α-Fe₂O₃@NC.



Fig. 8. Cyclic voltammograms of (a) α -Fe₂O₃, (b) α -Fe₂O₃@NC, the charge/discharge voltage profiles of (c) α -Fe₂O₃ (dash lines) and α -Fe₂O₃@NC (solid lines), rate performance of (d) α -Fe₂O₃ and α -Fe₂O₃@NC, and (e) cycling performance (discharge capacity) at a current density of 1000 mAg⁻¹, green dot shows its coulombic efficiency. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

capacity at 100 cycles was maintained at 603.8 mAh g^{-1} . In particular, the α -Fe₂O₃@NC composites exhibit good coulombic efficiency (CE) during cycling. The CE of the first cycle is 70% and 99% is maintained up to 20 cycles. This high coulombic efficiency represents a highly reversible lithium ion insertion/extraction in α -Fe₂O₃@NC composites electrodes [37].

Electrochemical spectroscopy (EIS) measurements were performed for detailed analysis of electrochemical performance. As can be seen in Fig. 9, the α -Fe₂O₃@NC composites in the intermediate frequency range at high frequencies are much smaller than the diameter of the semicircle of bare α -Fe₂O₃. The charge transfer resistance (Rcf) in the high frequency region is related to the size of the semicircle, and the semicircular size reduction in the composites is due to the high conductivity of the contained carbon in the α -Fe₂O₃@NC composites [17,21]. These results indicated lower contact and charge transfer resistance of α -Fe₂O₃@NC, due to the presence of carbon derived from microalgae, thus resulting in the highly enhanced electrochemical activity.

Furthermore, based on our results, along with the recent research on nitrogen doped carbon materials of anode in LIBs, we suggest the following possible cooperative effects between the N



Fig. 9. The Nyquist plots of the α -Fe₂O₃@NC and α -Fe₂O₃.

 Table 1

 Comparison of the performances used carbon materials derived from biomass as anode for LIBs.

Carbon source	Initial coulombic efficiency/%	Reversible capacity/ mAh g ⁻¹	Rate capability/ mAh g ⁻¹	Ref.
Microalgae	73 at	935 of 1st cycle and 902 of	954 at	This
	$1000{\rm mAg^{-1}}$	10th cycle at 200 mA g^{-1}	1Ag^{-1}	work
Wheat	62.9 at	502 of 1st cycle and 443.7	161.4 at	[50]
stalk	$37 { m mA g^{-1}}$	of 50th cycle at 37 mA g^{-1}	$3.72 \mathrm{Ag^{-1}}$	
Cotton	76 at	935 of 1st cycle at	240 at	[51]
cellulose	$50 { m mA} { m g}^{-1}$	$50 \mathrm{mA}\mathrm{g}^{-1}$	$2 \mathrm{A}\mathrm{g}^{-1}$	
Microalgae	79.5 at	445 of 1st cycle and 433 of	355 at	[26]
	$37 { m mA} { m g}^{-1}$	100th cycle at 37 mA g^{-1}	1Ag^{-1}	
Rice husk	49.8 at	393 of 1st cycle at	137 at	[52]
	$75 { m mA g^{-1}}$	$75 \mathrm{mA}\mathrm{g}^{-1}$	$3.75 \mathrm{Ag}^{-1}$	
Rice	48 at	986 of 1st cycle at	257 at	[53]
straws	$37.2 \mathrm{mA}\mathrm{g}^{-1}$	$37.2 \mathrm{mA}\mathrm{g}^{-1}$	$0.744\mathrm{Ag^{-1}}$	
Mangrove	65.7 at	524 of 1st cycle at	440 at	[54]
charcoal	$30 { m mA} { m g}^{-1}$	$30 \mathrm{mA}\mathrm{g}^{-1}$	$0.3 \mathrm{A}\mathrm{g}^{-1}$	
Spongy	59.5 at	450 of 1st cycle at	293 at	[55]
pomelo	$40{ m mAg^{-1}}$	$40 \mathrm{mA}\mathrm{g}^{-1}$	$0.32 \mathrm{Ag^{-1}}$	
peels				

dopants, carbon and Iron oxide in α-Fe₂O₃@NC toward anode in LIBs: (i) the microalgae as biomass can act as carbon support materials with the highly electrical conductivity as well as mesoporous (see Figs. 7 b and 9), thus it can not only promote electrochemical performance but also buffer volume expansion during charge/discharge reaction with Li⁺ [47–49]. (ii) the nitrogen, which is intrinsic in microalgae, is naturally doped to carbon materials. It is well-known that nitrogen doping can improve the electrochemical properties and promote more active site, leading the enhanced cycling performance [39]. Notably, the pyridinic (52.2%) nitrogen considered to be favorable for lithium insertions, due to increase number of defects, improving the capacity and transport of Li⁺. In Fig. 6 for XPS analysis, the nitrogen in α -Fe₂O₃@NC is estimated to be 3.61 at.%. Therefore, we believe that this microalgae as biomass is an effective way to provide an opportunity for advanced applications (see Table 1).

Conclusions

In this paper, α -Fe₂O₃@NC, the hybrid structure, is synthesized *via* spray pyrolysis. α -Fe₂O₃ nanoparticles uniformly distributed in

the biotemplate derived from green microalgae exhibit stable, excellent cycling performance compared to bare α -Fe₂O₃ due to enhanced conductivity and improved specific surface area. Successful fabrication of environmentally friendly α -Fe₂O₃@NC composites using the easy approach show the potential for designing high-performance anode materials and can be used as new anode materials for next-generation LIB, integrating TMOs with biomaterials.

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