# Capillary-Driven Formation of Iron Nanoparticles Embedded in Nanotubes for Catalyzed Lithium—Carbon Dioxide Reaction

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cells. We elucidate under varying thermal conditions the conversion mechanisms by which Fe nanoparticles are incorporated into CNTs by capillary force. Compared with pristine cells, Li-CO<sub>2</sub> cells employing Fe NPs@N-CNT catalysts deliver triple charge and discharge capacities, as well as stable cycle performance accompanied by lower charge polarization. By observing the reversible binding and disconnection between Fe and CO<sub>2</sub> during ex situ characterization, it was revealed that Fe nanoparticles act as catalyst components. Our suggested method focuses on rational designing of catalyst-embedded nanotube composites and highlighting their potential applications in advanced energy and environmental devices.

The increasing demand for fossil fuels has made environmental issues such as the greenhouse effect and consequent climate change serious global problems.<sup>1</sup> Substantial carbon dioxide (CO<sub>2</sub>) emissions from industry and vehicles have been deemed to be the main cause of global warming.<sup>2,3</sup> Carbon neutrality through the precipitous and compulsory reduction of fossil fuel usage is realistically unachievable; however, carbon capture and storage (CCS) is considered a promising post-cleaning solution for relieving CO<sub>2</sub> emission problems.<sup>4,5</sup> Chemical CO<sub>2</sub> capture utilizing amine-based absorbents has been traditionally employed; however, extending the traditional CCS technology to large-scale facilities requires significant amounts of energy and economic input.<sup>6-9</sup> Therefore, a breakthrough in CCS technologies by employing eco-friendly, easily controllable, and cost-effective methods is essential.

(Fe NPs@N-CNTs) via capillary action of hemoglobin solution, and their potential as catalytic electrodes for efficient Li-CO<sub>2</sub>

Electrochemical CCS platforms with Li-CO<sub>2</sub> battery architecture have been highlighted for their dual benefits of facilitating energy storage and environmental CO<sub>2</sub> fixation.<sup>10–14</sup> Li-CO<sub>2</sub> batteries operate on carbon dioxide (Mw of CO<sub>2</sub> = 44), a gaseous cathode material 2-fold lighter than transition-metal cathodes used in conventional lithium-ion batteries (i.e., Mw of LiCoO<sub>2</sub>  $\approx$  98), thereby achieving high gravimetric and volumetric energy densities for CO<sub>2</sub> storage and effectively satisfying the growing energy demands.<sup>15–17</sup> Since the one-way discharge reaction at high temperatures in Li-CO<sub>2</sub> cells is reported by Archer's group, several studies have been reported in recent years.<sup>7,18–25</sup> The electrochemical reaction between Li<sup>+</sup> and CO<sub>2</sub> (4Li<sup>+</sup> + 3CO<sub>2</sub> + 4e<sup>-</sup>  $\leftrightarrow$ 2Li<sub>2</sub>CO<sub>3</sub> + C, V<sub>0</sub> = 2.82 V) results in the formation and reverse decomposition of solid lithium carbonate products on the cathodic electrode.<sup>10</sup> Considering that insulating carbonate products irreversibly decompose during recharge, Li-CO<sub>2</sub> cell reaction kinetics could be enhanced by exploiting cathode catalysts with increased Coulombic efficiency and cycle numbers.<sup>26–28</sup> Catalysts that contain precious metals (e.g., Ru, Ir, Au) possess such properties; however, alternatives based on abundant and cost-effective elements are prospects for actualization in Li-CO<sub>2</sub> battery systems.<sup>29–33</sup>

Fe NPs@N-CN1

Calcination

Studies have highlighted biowaste as a sustainable, biodegradable, and profitable resource for catalyst materials,

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Figure 1. Schematic illustration of Fe NPs@N-CNT catalyst synthesis derived from hemoglobin blood protein and cycle process of discharge/charge reactions in Li-CO<sub>2</sub> cells with Fe NPs@N-CNT electrodes.



Figure 2. (a) Thermogravimetric analysis (TGA) of CNT and Fe NPs@N-CNT materials in an air atmosphere. (b) X-ray diffraction (XRD) patterns of CNT, Hb/CNT (before calcination), and Fe NPs@N-CNT (after calcination). (c) Raman spectra and X-ray photoelectron spectra (XPS) of CNTs, Fe NPs@N-CNTs for (d) C 1s, (e) Fe 2p, (f) N 1s, and (g) O 1s.

such as hemoglobin extracted from blood waste.<sup>15,34–37</sup> Hemoglobin molecules contain four globular protein groups, each enclosing a Fe ion in the center of a porphyrin called heme.<sup>38</sup> The Fe centered in the porphyrin participates in a redox reaction ( $Fe^{2+}/Fe^{3+}$ ) while combining with CO<sub>2</sub> on the hemoglobin histidine group, thereby utilizing hemoglobin as a catalyst component.<sup>15,39</sup> Furthermore, hemoglobin comprises diverse cations (e.g., iron) and anions (e.g., oxygen, nitrogen, carbon) and can be modified as a raw material and precursor to synthesize catalysts. Optimizing this procedure is expected to outperform current Li-CO<sub>2</sub> technology.

Here, we studied a novel method for synthesizing Fe NPs@ N-CNT catalysts for implementation in sustainable and efficient Li-CO<sub>2</sub> batteries (Figure 1). The Fe NPs@N-CNT catalyst materials were successfully fabricated via capillarydriven filtration procedure of hemoglobin–CNT (Hb/CNT) solution into the pore channel of CNTs, and subsequent thermal treatment of the mixture. The Hb/CNT solution successfully diffused into the CNT walls during filtration, and Fe nanoparticles with an average diameter of 5 nm were subsequently segregated after thermal treatment. In addition, N atoms from hemoglobin molecules were incorporated in CNTs as doping agents, to increase their electronic



Figure 3. (a-d) Scanning electron microscopy (SEM) images of CNT (panels (a) and (c)), and Fe NPs@N-CNT (panels (b) and (d)). (eg) Transmission electron microscopy (TEM) images of Fe NPs@N-CNT showing various structures of Fe nanoparticles embedded in CNTs. (h) Selected area electron diffraction (SAED) and (i-k) the corresponding TEM images of Fe NPs@N-CNT. (l) Scanning transmission electron microscopy (STEM) image and corresponding energy-dispersive X-ray spectroscopy (EDS) mappings of Fe NPs@N-CNT for (m) carbon, (n) iron, and (o) nitrogen.

conductivity. The structural and morphological characteristics of Fe NPs@N-CNTs were elucidated through material characterization processes. The capillary-driven formation of Fe NPs@N-CNT materials was further established by transmission electron microscopy (TEM) at varying thermal treatment states. Improved catalytic activities for both  $CO_2$ reduction reaction (CRR) and  $CO_2$  evolution reaction (CER) were achieved after employing Fe NPs@N-CNT catalysts in Li-CO<sub>2</sub> cells. The reversible formation/decomposition of discharge products during the discharge/charge process was verified via ex situ characterization. To summarize, besides introducing biowaste derived catalysts as potential alternatives for eco-friendly Li-CO<sub>2</sub> battery technology, this study provided

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Figure 4. TEM and (inset) fast Fourier transform (FFT) images obtained from (a) pristine and calcined Fe NPs@N-CNT samples at (b) 100, (c) 300, and (d) 500 °C. The TEM image of a nanoparticle in panel (b) seems to be aligned with ordered planes, but it only overlaps with the MWCNT behind. (e) Schematic diagram of capillary action, demonstrating the mechanism of Fe NP infiltration. (f) STEM image of tadpole-shaped Fe NPs (inset shows related EDS mapping).

new insights into hierarchical materials development and greenhouse gases reduction through  $CO_2$  fixation.

Fe NPs@N-CNTs were successfully synthesized via capillary-driven infiltration of a hemoglobin precursor into CNT pores and their subsequent calcination (Figure 1). We investigated the material characterizations of the Fe NPs@N-CNTs through various analysis platforms to comprehend the synthetic mechanism and structural features (Figure 2). Thermogravimetric analysis (TGA) of Fe NPs@N-CNTs (Figure 2a) examines the content of Fe species derived from the hemoglobin precursor, in comparison with pristine CNTs. In an air atmosphere, the carbon contents of both samples were oxidized and evolved to carbon dioxide at 400 °C. Consequently, substantial weight loss exceeding 85% was found between 400 °C and 600 °C. Unlike CNTs, Fe NPs@N-CNTs (11 wt %) remained after further heat processing as Fecontaining residue. The crystalline formation of CNT, Hb/ CNT, and Fe NPs@N-CNT samples was investigated via Xray diffraction (XRD). Similar peak signals of CNTs, Hb/ CNTs, and Fe NPs@N-CNTs were found at the same  $2\theta$ angles (Figure 2b), corresponding to the carbon and iron phases.<sup>34</sup> Hb/CNTs and Fe NPs@N-CNTs showed no additional peak compared with pristine CNTs, implying no further impurities and significant morphologic changes during the synthetic process (filtering, calcining, etc.). The overlapping peak positions for C (100) and Fe (110) at  $43^{\circ}$ , in conjunction with low Fe content, obscured the evidence for the presence of Fe. Therefore, we conducted Raman spectroscopy analysis to verify the molecular vibration information related to Fe species in Fe NPs@N-CNTs (Figure 2c). In both samples, distinct peaks of D (1350 cm<sup>-1</sup>) and G (1580 cm<sup>-1</sup>) bands associated with carbon species were observed.<sup>40</sup> The relative intensity of D and G bands  $(I_D/I_G)$ 

represents the structural modification of sp<sup>3</sup>-hybridized carbon atoms in CNTs.<sup>41,42</sup> The ratio of D and G bands in pristine CNTs and Fe NPs@N-CNTs was same as 1.3, suggesting that CNT backbones remained relatively undamaged during the capillary-driven infiltration of hemoglobin molecules and subsequent calcination process, which is consistent with XRD results. The additional vibration peaks below 1000 cm<sup>-1</sup> observed in Fe NPs@N-CNTs originated from the bonding of Fe particles with residual anion species (e.g., C, O, N) stemming from hemoglobin protein components. 43-45 To further understand detailed information regarding the surface and structural characteristics of pristine CNT and Fe NPs@N-CNT samples, X-ray photoelectron spectra (XPS) was performed (Figures 2d-g). CNTs and Fe NPs@N-CNTs presented common XPS spectra in C 1s corresponding to C-C, C-O, C=O, and O=C-O (Figure 2d), which subsequently corresponded to the XRD and Raman data (Figures 2b and 2c). The peak signals of Fe species are shown in the Fe 2p spectra (Figure 2e). The peaks of Fe  $2p_{1/2}$  (~720 eV) and Fe  $2p_{3/2}$  (~710 eV) confirm the existence of Fe nanoparticles in the synthesized Fe NPs@N-CNTs, despite their low content. Significant peaks in the N 1s spectra of Fe NPs@N-CNTs (Figure 2f) were also confirmed, implying that CNTs were doped with nitrogen atoms derived from hemoglobin proteins. Studies have shown that N doping agents effectively enhance the electronic conductivity of carbon materials.<sup>46–50</sup> The analogous peaks of O 1s spectra in pristine and Fe NPs@N-CNTs implied negligible oxygen involvement in the synthetic process, excluding the Fe and N sources. The functional incorporation of foreign Fe and N elements is expected to enhance the catalytic and electronic properties of Li-CO<sub>2</sub> cells.



Figure 5. (a) Cycle voltammetry (CV) curves of Li-CO<sub>2</sub> batteries with a pristine electrode (CNT) under Ar and CO<sub>2</sub> atmospheres. (b) CV curves of Li-CO<sub>2</sub> cells based on a pristine electrode and the Fe NPs@N-CNT containing electrode. (c, d) Discharge/charge curves of the CNT and Fe NPs@N-CNT electrode under Ar and CO<sub>2</sub> atmospheres. Cycling performance of Li-CO<sub>2</sub> batteries (e) without Fe NPs@N-CNTs and (f) with Fe NPs@N-CNTs in the 4.5–2.3 V voltage window under the specific capacity limit of 600 mA h  $g_{carbon}^{-1}$  at a current density of 100 mA  $g_{carbon}^{-1}$ . The electrolyte was 1 M LiTFSI in TEGDME.

The surface morphology and detailed internal features of Fe NPs@N-CNTs were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The conformation of CNT (yellow) and Fe NPs@N-CNT (blue) are almost similar in shape and size (Figures 3a–d). The congruent exterior morphologies of the samples indicate the prevention of unexpected impurities and/or segments during fabrication, excluding any segregated hemoglobin

residue. In contrast, the interior of Fe NPs@N-CNTs exhibited a nanoparticle-embedded nanotube shape, compared with pristine CNTs. It can be found from Figure 3e and Figure S1 in the Supporting Information that particles are discretely centered in hollow part of multiwalled CNT (MWCNT). The nanoparticles dispersed within the tubes exhibited various morphologies, such as spheres (Figure 3f) and ellipses (Figure 3g). The particle sizes varied, but without exceeding 20 nm.

Furthermore, they were immobilized in numerous CNT walls while tilting or bending the neighboring layers according to their shape, verifying the particles' placement in the CNT's interior rather than the surface. In the selected area electron diffraction (SAED) pattern (Figure 3h), ring patterns indexed to the (002) and (100) planes of carbon can be observed. Additional spot patterns belonging to Fe were detected and are associated with a single crystalline phase along the (110) lattice. The lattice distances of carbon nanotubes and Fe nanoparticles were also confirmed by SAED pattern results (Figures 3i-k). Boxes denoted as A and B are related to the (002) plane of carbon nanotubes (3.39 Å) and (110) plane of Fe particles (2.02 Å), respectively. To further confirm the presence of embedded Fe nanoparticles within CNTs, we performed energy-dispersive X-ray spectroscopy (EDS) mapping, which confirmed the presence of C, Fe, and N (Figures 31-o). In accordance with the predominant distribution of carbon elements, excessive spots of Fe (Figure 3n) were gathered locally in the CNT middle. Moreover, the uniform distribution of nitrogen (Figure 30) implied that the CNT was homogeneously doped with nitrogen originating from hemoglobin protein, which is consistent with XPS results (Figure 2f).

We assume two possibilities for the successful synthesis of Fe NPs@N-CNTs by simple filtration of a hemoglobin/CNT mixture solution and subsequent thermal treatment: (i) Fe sources in hemoglobin are diffused through CNT walls, and (ii) the hemoglobin solution is directly inserted into CNTs during the filtration process. TEM images and corresponding fast Fourier transform (FFT) images of Fe NPs@N-CNT materials (Figures 4a-d) collected at different calcination temperatures further elucidate the synthetic mechanism of our novel Fe NPs@N-CNTs. CNT powder is dispersed into a hemoglobin solution, which was subsequently filtrated (Figure 4e). We performed ex situ TEM analysis on the as-prepared and calcined Hb/CNT samples at different temperatures (100, 300, and 500 °C) to observe the morphological and structural evolution of Fe nanoparticles in the CNT wall. Interestingly, the nanoparticle residues were found even in the as-prepared Hb/CNT samples obtained from the filtration process without thermal treatment, implying that the hemoglobin solution directly infiltrated the CNTs during the process. The particles within could be segregated by beam damage during TEM analysis. We believe that Fe atoms are rarely diffused without penetrating the walls of CNTs. A single molecule of solid hemoglobin protein is under 5 nm in size; therefore, dissociated hemoglobin species in the aqueous solution can be sufficiently inserted in CNTs through their 10-nm pores.<sup>51</sup> Besides two ring patterns related to the carbon source (Figures 4a and 4b), no FFT (inset) spot signals were observed in the pristine and calcined at 100 °C samples. No SAED patterns of Fe particles related to the existence of crystalline structure were observed, indicating an amorphous or glassy phase. After calcination at temperatures above 300 °C, FFT images indicate spot signals corresponding to the (110) plane of Fe, implying amorphous Fe particles converting to the crystalline phase (Figure 4c). In addition, symmetrical dots indexed on the (220) plane of Fe were detected, implying the strengthening of nanoparticle crystallinity following thermal treatment at 500 °C (Figure 4d). Through a simple scheme, we demonstrate the synthetic process of Fe NPs@N-CNTs via capillary-driven infiltration of hemoglobin solution into CNTs, and subsequent thermal treatment (Figure 4e). Capillary-driven nanotechnology using CNTs has been utilized in other fields, such as drug delivery, nanoelectronics, nanomedicine, etc.<sup>52–60</sup> The forceup description of capillary pressure ( $P_c$ ) can be described from the Young–Laplace equation,

$$P_{\rm c} = 2\gamma \left(\frac{\cos\theta}{r_{\rm c}}\right)$$

where  $\gamma$  is the interfacial tension,  $r_c$  the effective radius of the interface, and  $\theta$  the wetting angle of the liquid on the surface of the capillary.<sup>61</sup> The significantly small diameters ( $r_c \approx 5$  nm) of carbon nanotubes provide potent capillary forces, capable of drawing the solvent into the tubes by capillary pressure.<sup>62–64</sup> The vacuum pump generated capillary force and turbulence flow can sufficiently absorb water-dissolved hemoglobin molecules into CNT voids. The electron beams generated from TEM observation damaged the as-prepared Hb/CNT solution, eliminating protein components, and leaving an iron residue. Therefore, iron particles can be detected within CNTs in all phases of TEM, regardless of calcination temperature.

As another evidence of capillary action in Fe NPs@N-CNTs, unique-shaped Fe particles, tadpole-shaped Fe NPs, were observed from TEM analysis (see Figure 4f and Figure S2 in the Supporting Information). The EDS mappings of the tadpole-shaped NPs confirmed that they consisted of Fe. Furthermore, the Fe traces strongly indicated that hemoglobin solution entered the CNTs via capillary action, and the Fe residues were fixed inside the CNTs after subsequent thermal treatment. The aforementioned results indicated that the capillary force was introduced during the synthesis of Fe NPs@ N-CNTs, drawing the hemoglobin solution inside.

CO<sub>2</sub> known as a greenhouse gas can be captured and stored in electrochemical Li-CO<sub>2</sub> cells to be utilized as a gaseous cathode material, accurately controlling reaction amounts under the Faradaic law of electrolysis (m = QM/Fz, where m is the mass of the product substance, Q the total electric charge, F the Faraday constant, M the molar mass of the substance, and z the number of electrons transferred per ion).65 We introduced Fe NPs@N-CNTs as air electrode catalysts in Li-CO<sub>2</sub> cells to boost reaction kinetics, and evaluate their electrochemical performance (Figure 5). Prior to the above process, we performed cyclic voltammetry (CV) tests on Li-CO<sub>2</sub> cells by using a pristine CNT electrode under Ar and CO<sub>2</sub> atmospheres (Figure 5a). In an inert atmosphere (Arpurged), the cell exhibits negligible reactive and electrochemical performance (Figure 5a and Figure S3 in the Supporting Information), whereas, in a  $CO_2$  atmosphere, lithium reacts electrochemically with carbon dioxide  $(4Li^{+} +$  $3CO_2 + 4e^- \leftrightarrow 2Li_2CO_3 + C)$ , thereby increasing the current in the cathodic and anodic regions. The onset potentials of CO<sub>2</sub> purged cell were 2.7 V in CRR and 3.6 V in CER. To evaluate improvements after introducing Fe NPs@N-CNT catalysts, we performed CV tests on Li-CO<sub>2</sub> cells containing both pristine CNT and Fe NPs@N-CNT electrodes (see Figure 5b, as well as Figure S4 in the Supporting Information). The potential difference between onset potentials of CRR (3.1 V) and CER (3.4 V) was 0.3 V, three times lower, compared with CNT (0.9 V), indicating the enhanced cell reversibility induced by Fe NPs@N-CNT catalysts for both discharge and charge reactions. The additional peak observed at 2.9 V in the cathodic region could be related to the one-way reduction of Fe nanoparticle catalysts. For the anodic region, an increase of current after 3.4 V, corresponding to CO<sub>2</sub> evolution, is



Figure 6. Ex situ measurements on carbon dioxide electrodes. SEM images obtained from (a) pristine, (b, c) discharged, and (d) charged electrodes. (e, f) Ex situ TEM images of Fe NPs@N-CNTs after discharge. (g) XRD peaks obtained from pristine, discharged, and charged electrodes. XPS spectra obtained from each stage of electrodes collected in the (h) C 1s, (i) Li 1s, (j) O 1s, and (k) Fe 2p.

significantly catalyzed, in comparison with pristine. Therefore, the CV results verify the catalytic effects of Fe NPs@N-CNTs in the Li-CO<sub>2</sub> cell for both discharge (cathodic) and charge (anodic) reactions.

To further investigate the electrochemical performance of Li-CO<sub>2</sub> cells with Fe NPs@N-CNT catalysts, we conducted discharge/charge tests using electrodes in varying purging gases (see Figures 5c and 5d). The cell employing Fe NPs@N-CNTs (see Figure 5c and Figure S5 in the Supporting Information), correspondingly to pristine CNTs (Figure S3), underperformed with Ar, exhibiting a low discharge/charge capacity of 486 mAh  $g^{-1}$ . In contrast, the capacity following  $CO_2$  purging increased to 3898 mAh g<sup>-1</sup> for discharge and 3482 mAh  $g^{-1}$  for charge, corresponding to a Coulombic efficiency of 90%, indicating improved performance, compared with pristine CNTs (discharge capacity = 1206 mAh  $g^{-1}$ , charge capacity: =  $1062 \text{ mAh g}^{-1}$  (Figure 5d). In addition, Fe NPs@N-CNT cells exhibited lower voltages in the charge region, compared with pristine CNTs, implying overpotential reduction. The results verify the reversible reaction between Li ions and CO<sub>2</sub> gas, facilitated by Fe NPs@N-CNT catalysts. In the first discharge curve of CNTs and Fe NPs@N-CNTs under

 $CO_2$  atmosphere, an additional plateau at 3.0 V was observed for Fe NPs@N-CNTs (Figure 5d). It is theorized that the high voltage plateau stems from the reductive reaction between Fe catalysts and  $CO_2$ , which is consistent with the peak at 2.9 V in the CV results (Figure 5b).

In addition, to determine whether the catalytic effects of Fe NPs@N-CNTs were attributed to the Fe NPs embedded in CNTs or doped N heteroatoms, we fabricated N-doped CNTs (N-CNTs) and performed electrochemical cell tests with N-CNT cathodes. N-CNTs were fabricated using melamine, a well-known N-containing organic compound, as the precursor, and their properties are presented in Figures S6 and S7 in the Supporting Information. No significant impurities were present in the fabricated N-CNTs, and the doped N atoms were wellspread and aligned along the CNTs. In addition, we conducted an electrochemical test featuring an N-CNT cathode (see Figure S8 in the Supporting Information). The discharge capacity of the N-CNT-based cell was higher than that of the pristine CNT-based cell, indicating that N-doping boosted the catalytic properties of N-CNTs for the CO<sub>2</sub> reduction reaction. However, during subsequent charge processes, the charge capacity of the N-CNT-based cell was poor (163 mAh  $g^{-1}$ )

and its overpotential was high. Although N-doping can affect cell performance, the overall catalytic properties of the Fe NPs@N-CNTs were attributed to the Fe NPs. The synergistic effects of both doped N heteroatoms and Fe NPs were reflected in the performance of a cell featuring a Fe NPs@N-CNT cathode.

Figures 5e and 5f depict the charge/discharge profiles of pristine CNTs and Fe NPs@N-CNTs in CO2, respectively, collected at various cycle numbers with capacity limits. Both cells performed stable over the 30th cycle without a decline in capacity. Nevertheless, the pristine CNT electrode showed highly polarized profiles at the beginning of the charge process, which remained until the 30th cycle with no other specific changes; diversely, the cells with Fe NPs@N-CNT catalysts exhibited a gradual decrease in voltage, resulting in charge polarization reduction. Unless sharing a similar curve shape with pristine CNTs from the first cycle, Fe NPs@N-CNTs charge voltage continuously declines until the 15th cycle, where a slight increase is exhibited, but constantly remaining below pristine cells. This observation implies reduced energy loss for cell operation. The catalytic effect was demonstrated in further ether-based electrolytes (i.e., diethylene glycol diethyl ether (DEGDME)) by employing the same cycling experiment (see Figure S9 in the Supporting Information). Although possessing an inferior cycle life to TEGDME, the catalyst promoted advanced capacity and long cyclability with diminished overpotentials. In summary, Fe NPs@N-CNTs constitute advantageous Li-CO<sub>2</sub> battery catalysts, facilitating the reverse decomposition of discharge products with decreased overpotentials.

To further examine Li-CO<sub>2</sub> cell reversibility, we conducted ex situ characterizations using diverse surface and structural analysis tools. The morphological appearance of electrodes at variable electrochemical states was analyzed by SEM (Figures 6a-d). Pristine electrodes exhibited uneven shapes, presenting the complex of Fe NPs@N-CNTs and binder on the Ni foam substrate (Figure 6a). After a discharging process, we detected the planar surface covered by carbonate-based discharge products (Figures 6b and 6c), and reversibly recovered the initial uneven shape of pristine cells following charge (Figure 6d). Moreover, we analyzed the morphologies of the products by ex situ TEM analysis (Figures 6e and 6f and Figure S10 in the Supporting Information). The thin discharge products were uniformly formed on the CNT surface, as marked by the white arrows. The products were also observed on the inner walls of CNTs, as indicated by the yellow arrows. This observation was apparently attributed to the infiltration of electrolyte and CO<sub>2</sub> gas into the CNT pore. The formation of discharge products simultaneously occurs on the outer surface and inner walls of CNTs. Furthermore, the ex situ XRD pattern (Figure 6g) indicated the complete disappearing of Li<sub>2</sub>CO<sub>3</sub> discharge products formed on the electrodes during the subsequent charge process, confirming that the possible reaction in the Li-CO<sub>2</sub> cell is closer to the formation of Li<sub>2</sub>CO<sub>3</sub> phase (4Li<sup>+</sup> + 3CO<sub>2</sub> + 4e<sup>-</sup>  $\leftrightarrow$  2Li<sub>2</sub>CO<sub>3</sub> + C), rather than the formation of oxalates  $(2Li^+ + 2CO_2 + 2e^- \leftrightarrow 2Li_2C_2O_4)$ . These results are consistent with our previous observation regarding the discharge product structure.<sup>15</sup> The peak feature of  $Li_2CO_3$ seems relatively weak, implying amorphous characteristics. To examine the surface changes of the electrodes involving Fe NPs@N-CNT catalysts, we performed ex situ XPS (see Figures 6h-k and Figure S11 in the Supporting Information) and Raman spectroscopy (Figure S12 in the Supporting electrodes. We dipped the pristine electrode sample into an electrolyte solution for further comparison with the discharged and charged electrodes. In the C 1s spectra, the peak intensity related to lithium bis(trifluoromethanesulfonyl)imide (LiTF-SI) salts increased after discharge, because of the integration of salts and other electrolyte components (e.g., solvents) with discharge products (Figure 6h). As the cells progress, the C-Oand C-C peaks remain inversely proportional. During the discharge process, the discharge products (Li<sub>2</sub>CO<sub>3</sub>) were formed  $(4Li^+ + 3CO_2 + 4e^- \rightarrow 2Li_2CO_3 + C)$  and the C-O peak grew accordingly. While synthesized Li<sub>2</sub>CO<sub>3</sub> is decomposed into Li ions, carbon dioxide  $(CO_2)$ , and oxygen  $(2Li_2CO_3 \rightarrow 4Li^+ + 2CO_2 + O_2 + 4e^-)$ , the oxygen could be bound to nearby carbon and form C-O structures.<sup>66-68</sup> The decomposition of Li<sub>2</sub>CO<sub>3</sub> can be proved by the diminished peaks in C 1s, Li 1s, and O 1s. The peak appearing in the Li 1s spectrum (Figure 6i) indicates Li<sub>2</sub>O to be an intermediate product of  $Li_2CO_3$  chemical dissociation ( $Li_2CO_3 \rightarrow Li_2O +$  $CO_2$  or  $Li_2CO_3 + C \rightarrow Li_2O + CO)$ , which dissolves completely during charge.<sup>15</sup> The XPS spectra of O 1s and Fe 2p (Figures 6j and 6k) clarified the catalytic behavior of Fe elements in Fe NPs@N-CNTs. After discharge, the peak intensity corresponding to Fe-O-C was reduced while the Fe<sup>0</sup> peak occurred, verifying that Fe elements participated in the electrochemical reaction as redox catalysts. As Li-CO<sub>2</sub> cells were being purged, Fe particles in Fe NPs@N-CNTs were bound to oxygen in CO<sub>2</sub>. CO<sub>2</sub> is a nonpolar molecule; however, the strong electronegativity of Fe drew the molecular orbitals of CO<sub>2</sub>, inducing temporary dipole moments and forming weak bonds of Fe-O-C. The bonds were broken during discharging, with the released CO<sub>2</sub> combining with Li to form Li<sub>2</sub>CO<sub>3</sub>. The left Fe particle became metallic, explaining the Fe<sup>0</sup> peak in the Fe<sup>2</sup>p spectra. The metallic Fe reverted to Fe-O-C bonds after charging, and the reactions continued as the cycle progressed. Despite the various alterations in the chemical bonds between Li, C, O, and Fe during discharge and charge, the N 1s spectra remained relatively unaltered (Figure S11 in the Supporting Information), indicating no direct involvement of N elements in electrochemical reactions, therefore implying their sole contribution as functional doping agents in CNTs, enhancing their conductivity. Summarizing, we report N-doped CNTs with Fe nano-

Information) on the pristine, discharged, and charged

particles derived from hemoglobin biomolecules as catalyst candidates for enhancing the performance of Li-CO<sub>2</sub> batteries. Through simple and novel procedures based on the strong capillary motion of hemoglobin solution into narrow nanotube pores, we successfully embedded Fe nanoparticles in multiwalled CNTs and highlighted their multiple configurations. We successfully verified the synthetic mechanism by morphological and structural observations of the fabricated Fe NPs@N-CNTs at different calcination temperatures. Compared with pristine cells, Li-CO<sub>2</sub> cells employing Fe NPs@N-CNT catalysts delivered increased discharge/charge capacities and stable cyclability with low charge overpotentials. We confirmed the reversible formation and decomposition of lithium carbonate products by ex situ characterizations. Furthermore, we revealed that Fe NPs@N-CNTs can act as efficient catalytic agents by forming Fe-O-C bonds during the Li-CO<sub>2</sub> reaction, with a reversible phase transition and redox of Fe elements after discharge (metallic state, Fe<sup>0</sup>), and charge (bound state, Fe-O-C). This study suggests a straightforward and effective

method to embed nanoparticles in nanotubes using capillary force, which can be widely utilized in nanomaterial synthesis. Moreover, we proposed new approaches for developing green catalysts for energy and environmental storage platforms using recycling nature-extracted materials.

### ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmaterialslett.1c00078.

Experimental details of the synthetic procedures; TEM images and EDS mappings of Fe NPs@N-CNTs collected at different areas; full discharge/charge tests of CNT and N-CNT electrodes; CV tests of CNT and Fe NPs@N-CNT electrodes; TEM images, EDS mappings and XPS data of N-CNTs; c performance of the Li-CO<sub>2</sub> batteries in DEGDME electrolyte; XPS and Raman data of Fe NPs@N-CNTs (PDF)

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#### **Author Contributions**

The manuscript was written through contributions of all authors.

#### Notes

The authors declare no competing financial interest.

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