

# Mesoporous carbon nitride loaded with Pt nanoparticles as a bifunctional air electrode for rechargeable lithium-air battery

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**Abstract** A composite comprised of oxygen reduction reaction (ORR) catalyst and oxygen evolution reaction (OER) catalyst was designed and applied as a bifunctional electrocatalyst for the air electrode of the lithium-air battery. The ordered mesoporous carbon nitride (MCN) prepared by a nano hard-templating approach displayed a surface area as high as  $648 \text{ m}^2 \text{ g}^{-1}$  and a large pore volume of  $0.7 \text{ cm}^3 \text{ g}^{-1}$  and acted as both the ORR catalyst and the support for the in situ-formed OER catalyst of Pt particles with a diameter of 3–4 nm. The electrochemical performances of the electrode were examined in a solid-state lithium-air cell structured as Li/LATP-based electrolyte/cathode, which demonstrated a higher round-trip efficiency and lower overpotential compared with the Pt@AB and MCN electrodes. The combination of the OER and ORR catalysts is proved as an effective way to improve the performance of lithium-air batteries.

**Keywords** Mesoporous carbon nitride · Pt · Air electrode · Lithium-air battery

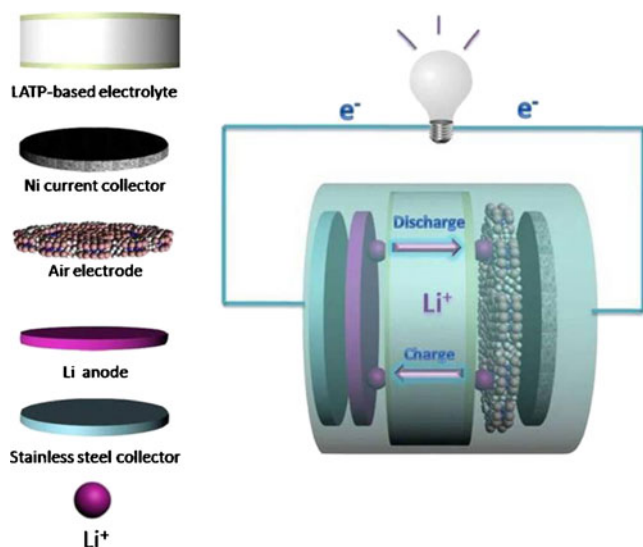
## Introduction

Significant attention has been given to electrochemical batteries, the alternative, sustainable, and environmentally friendly systems for energy storage and conversion. Among them, the lithium-air battery has captured worldwide attention recently because of its ultrahigh specific energy density

of  $11,140 \text{ Wh kg}^{-1}$  rivaling that of gasoline. One of the most prominent advantages of the lithium-air battery is that the cathode active material, oxygen, does not need to be stored in the battery but from the inexhaustible air which leads to high energy density and low cost of the practical battery [1–3]. Four chemical architectures of the lithium-air battery have been proposed, i.e., aqueous lithium-air battery which was reported early in 1976 by Littauer [4], aprotic lithium-air battery proposed by Abraham and Jiang and developed by a lot of groups [1, 5, 6], all-solid-state Li-air batteries illustrated by Kumar et al. [7, 8], and hybrid (non-aqueous/aqueous) lithium-air battery [9, 10]. Among the four architectures, the all-solid-state design eliminated the usage of liquid electrolyte and avoided the evaporation and safety concerns of liquid electrolyte. Unfortunately, its reversibility is poor, and voltage polarization is serious because of the slow kinetics of electrochemical reactions of oxygen in the battery. The air electrode kinetics has been considered as one of the most critical factors that restricted the electrochemical performances of the Li-air battery. Many particular air electrode structures were therefore designed to improve the cell performances. A bifunctional electrocatalyst for effective oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) was ever proved by Lu et al. as an effective way [16].

Herein we developed a new bifunctional air electrode with mesoporous carbon nitride as the support and Pt nanoparticles as the catalyst. Compared with various carbon support [11–14], the incorporation of nitrogen atoms in the carbon nanostructure introducing lots of lone pair electrons awards mesoporous carbon nitride (MCN) an improved inherent oxygen reduction activity benefiting to ORR kinetics [15]. Moreover, Pt has been reported as the most active catalyst for OER among Pt, Au, and C in bulk and nanoparticle forms [16]. We combined MCN and Pt and used it

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**Fig. 1** Scheme of the configuration of the solid-state lithium-air battery

as a bifunctional air electrode in the lithium-air battery for the first time. As expected, mesoporous carbon nitride with ordered mesoporous structure, high specific surface area, and large pore volume was successfully prepared, and Pt nanoparticles with a diameter of 3–4 nm were in situ synthesized on the MCN support. The electrochemical performances of the electrodes were examined with an all-solid-state Li-air battery, and improved results with good round-trip efficiency (a high discharge voltage and a low charge voltage) as high as 87% were obtained.

## Experimental

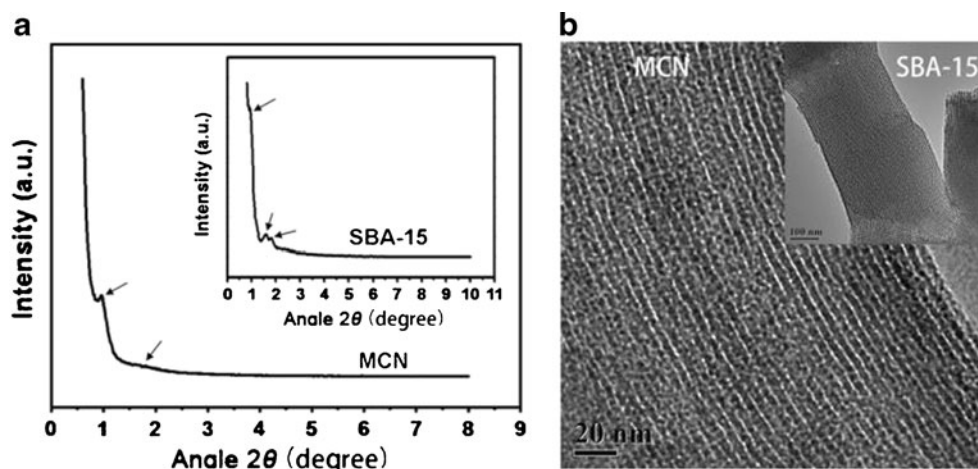
MCN was synthesized by a nano hard-templating approach as reported by Vinu [17] using SBA-15 as a template, ethylenediamine (EDA) as nitrogen source, and carbon tetrachloride

(CTC) as carbon source. And the template SBA-15 was prepared according to the typical procedure developed by Zhao et al. [18] using tetraethyl orthosilicate as a silica source and P123 amphiphilic triblock copolymer as the structure-directing agent. The synthesis of MCN was performed as follows: the prepared SBA-15 (1 g) was added to the mixture of EDA (2.7 g) and CTC (6 g), refluxed, and stirred at 90 °C for 6 h. And then, the obtained dark brown-colored solid mixture was dried in a drying oven at 80 °C for 12 h, ground into fine powder, and calcined in a nitrogen flow at 600 °C for 5 h. Finally, the silica framework was removed in 5 wt.% hydrofluoric acid, and MCN was obtained after filtration, washing several times with ethanol, and dried at 60 °C.

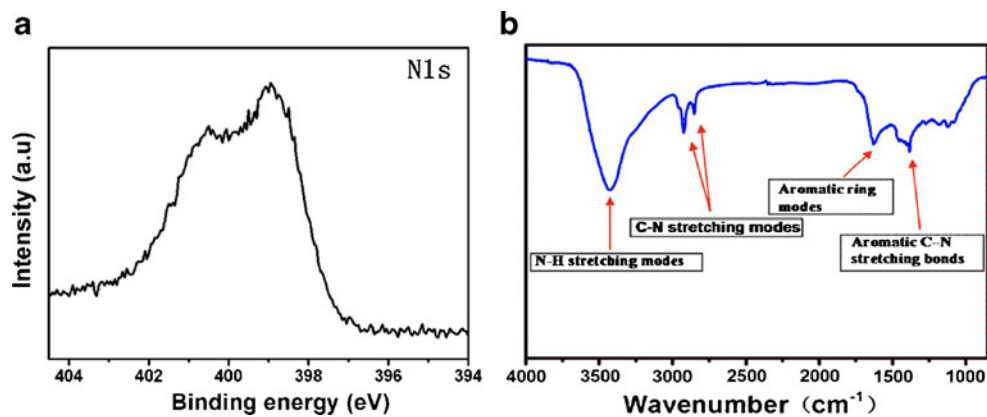
Then, Pt nanoparticles were dispersed in situ on both MCN and acetylene black (AB) supports according to a traditional process [19]. During the preparation process of Pt@MCN and Pt@AB composites, the same amount of  $\text{H}_2\text{PtCl}_6$  (0.25 g) and equal weight of supports (0.15 g) were used.

The air electrodes for charge and discharge tests were prepared by spreading a mixture of the electrode materials including catalysts (Pt@MCN, Pt@AB, MCN, respectively), conductive agent (AB), and binder (PVDF) with weight ratio of 60:20:20 to a nickel foam. The use of AB is to rule out the impact of conductivity on the battery performance as mentioned earlier [11]. The electrochemical performances of the electrodes were examined in a modified solid lithium-air battery with configuration as indicated in Fig. 1. A highly Li-ion conductive LAMP ( $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ ) electrolyte membrane with ionic conductivity higher than  $1.0 \times 10^{-4} \text{ S cm}^{-1}$  combined with two gel-type interface membranes was applied as the solid separator to protect lithium from air. The preparation process and properties of the LAMP material have been reported elsewhere [20]. All of the batteries worked directly in the air atmosphere.

**Fig. 2** Small-angle x-ray diffraction patterns (a) and TEM images (b) of the prepared MCN material and its template SBA-15 (inset)



**Fig. 3** XPS (a) and FT-IR (b) spectra of the prepared MCN material



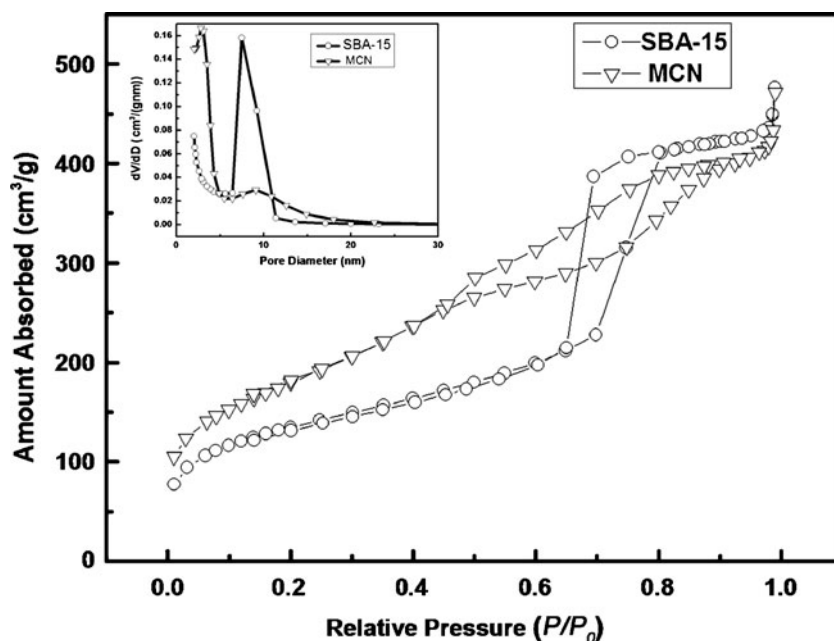
## Results and discussion

Small-angle x-ray diffraction was used to examine the pore-structure ordering of the prepared MCN material along with the parent SBA-15 template. As Fig. 2a indicated, the SBA-15 template (inset) exhibited three well-resolved peaks that can be indexed to a two-dimensional hexagonal lattice. Similar to the XRD pattern of the parent SBA-15 template, two well-resolved peaks of the prepared MCN material demonstrated that it has successfully replicated the two-dimensional hexagonal ordered mesoporous structure of the SBA-15 template, which was further confirmed by the comparison of TEM images of the prepared MCN material with its parent SBA-15 template as Fig. 2b indicated. In Fig. 2b, the obtained MCN exhibited several hundred nanometer long, uninterrupted, and uniform pore channels, exactly the same with the SBA-15 template as the inset of Fig. 2b indicated. And its two-dimensional hexagonal ordered mesoporous structure would

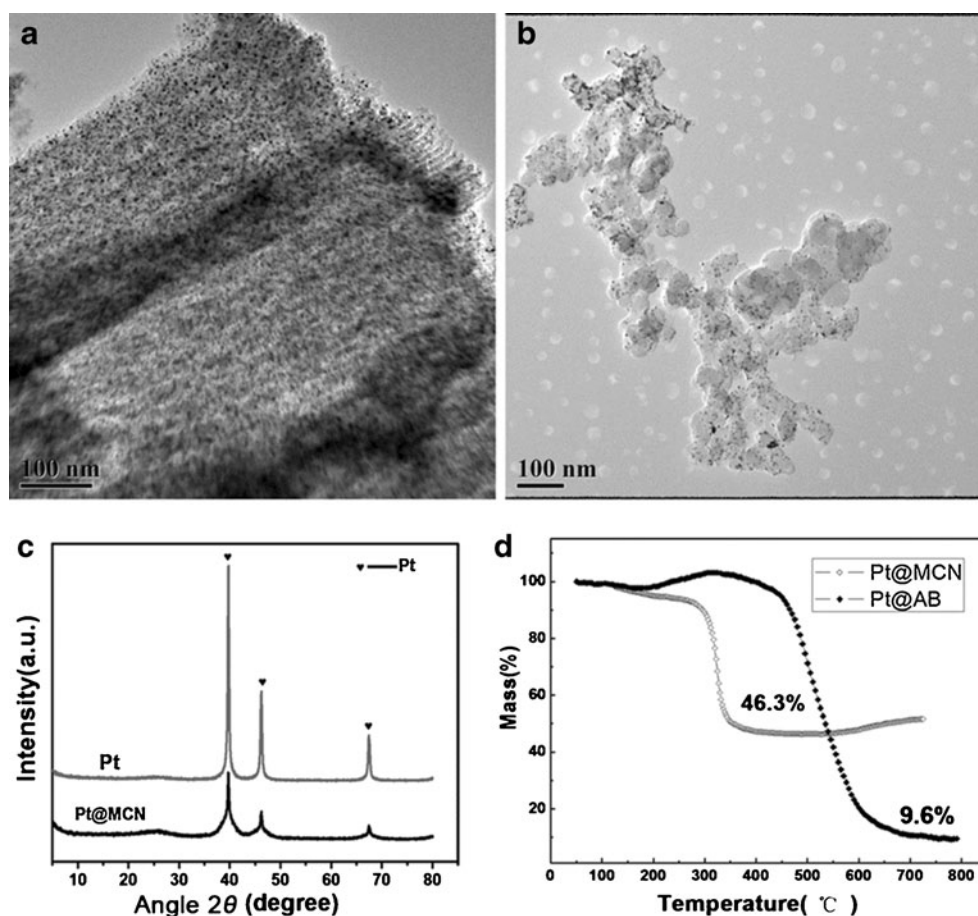
be beneficial to the dispersion of Pt nanoparticles and the catalytic reaction of oxygen.

Figure 3 showed the x-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FT-IR) spectra of the MCN material. The presence of two peaks at about 397.8 and 400.2 eV revealed that the existence of nitrogen atoms bonded with the graphitic carbon atoms, and nitrogen atoms trigonally bonded to all  $sp^2$  carbons or bonded with the  $sp^2$  carbon atoms and hydrogen atoms, respectively. And the amount of nitrogen calculated from the XPS analysis is about 15.11%. Moreover, the FT-IR spectrum also confirms the presence of aromatic C–N stretching bonds, aromatic ring modes, C–N stretching bonds, and the stretching mode of the N–H groups in the aromatic ring. Similar results were also obtained in the nonporous carbon nitride samples [15, 17, 21]. In a word, MCN material with high nitrogen content and graphite-like  $sp^2$  bonded structure has been successfully obtained.

**Fig. 4** Nitrogen adsorption–desorption isotherms and BJH pore size distributions (inset) of the SBA-15 template (white circles) and the obtained MCN material (white inverted triangles)



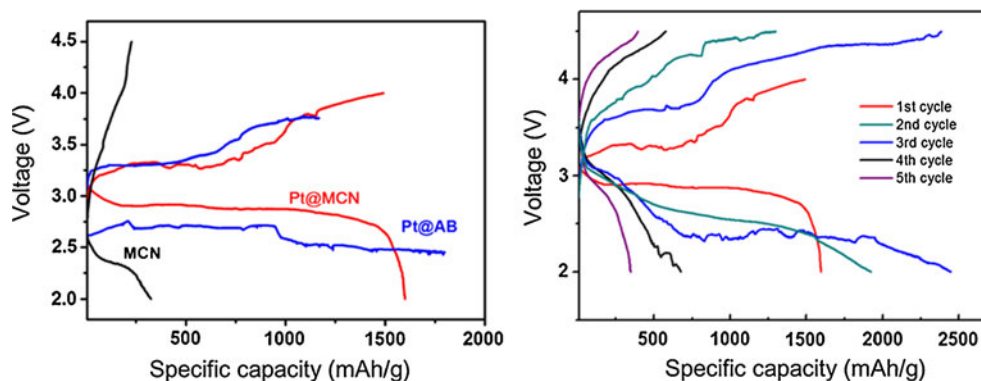
**Fig. 5** TEM image of Pt nanoparticles dispersed on MCN (a) and AB (b) support; c XRD patterns of Pt and Pt@MCN material; d TG curves of Pt nanoparticles dispersed on MCN (white diamonds) and AB (black diamonds)



Nitrogen adsorption–desorption measurement was used to further examine the textural parameters of the prepared materials. The isotherms of the prepared template and MCN material as Fig. 4 indicated both belong to typical IV-type curves corresponding to mesopore structure. Even better results are that the obtained MCN material exhibited a larger specific surface of  $648 \text{ m}^2 \text{ g}^{-1}$ , a huge pore volume of  $0.7 \text{ cm}^3 \text{ g}^{-1}$ , and a diameter of 4.7 nm according to the nitrogen adsorption branch. Compared with the traditional AB support with a specific surface of  $38.422 \text{ m}^2 \text{ g}^{-1}$ , a large amount of Pt nanoparticles has dispersed in the mesopore

channels of MCN compared with AB support as the TEM images of Fig. 5a and b indicated. And the XRD patterns in Fig. 5c proved the presence of Pt nanoparticles on MCN support. Furthermore, the comparison of thermogravimetric (TG) curves of MCN loaded with Pt nanoparticles and AB loaded with Pt nanoparticles in Fig. 5d demonstrated that the amount of Pt dispersed on MCN (46.3%) is almost five times that on AB (9.6%), suggesting that MCN is a promising support candidate for an air electrode with a highly efficient use of expensive Pt source. Besides, traditional carbon support is not necessary anymore for Pt@MCN

**Fig. 6** Charge and discharge curves of the first cycle of the prepared air electrodes at a current density of  $0.02 \text{ mA cm}^{-2}$  (a) and the cycling performance of Pt@MCN electrode at a current density of  $0.02 \text{ mA cm}^{-2}$  (b)



which would greatly reduce the weight of the electrode toward high energy density of the Li-air cell.

In order to understand the roles that Pt and MCN played in Pt@MCN air electrode in catalyzing the ORR and OER reactions, we compared the first discharge and charge profiles of the Li-air batteries with the three kinds of air electrodes in Fig. 6a. As expected, the Pt@MCN electrode showed the highest round-trip efficiency of up to 87% with the highest discharge voltage at around 2.87  $V_{Li}$  and the lowest charge voltage at about 3.30  $V_{Li}$  below 50% capacity among these three kinds of electrodes. And this round-trip efficiency is higher than a previous report [16], indicating that the Pt@MCN-based air electrode has excellent catalytic performance for both OER and ORR kinetics. During charge process, comparable charge voltages were found between the Pt@MCN and Pt@AB electrodes, which indicates the effect of Pt nanoparticles responsible for the OER kinetics [16]. While during discharge process, the Pt@MCN air electrode showed a much higher discharge voltage than the other two air electrodes, indicating its much better ORR catalytic activity. The remarkable effects of the Pt@MCN composite are assumed to be owing to the possible synergistic interaction between Pt nanoparticles and the MCN matrices, which is especially beneficial to the catalytic activity of MCN for ORR. The mechanisms need to be further studied in the future. What is more, the cycling performance of the Pt@MCN electrode showed a quite good capacity retention after three cycles as Fig. 6b indicated. But a large voltage polarization happened after the first cycle which was a common phenomenon in the lithium-air batteries reported. Through the mechanisms being investigated, we speculate that the oxidation of catalysts by high-energy oxygen atoms generated by the decomposition of the discharge products during charge process and the lack of the intimate contacts of the deposited discharge products with the catalysts [22] could be the main reasons.

## Summary

A bifunctional air electrode with MCN as the support and Pt nanoparticles as the catalyst has been successfully prepared. The composite exhibited excellent electrochemical performances in an all-solid-state Li-air battery, delivering about 50% of the discharge capacity above 2.87  $V_{Li}$  and about 50% of the charge capacity below 3.30  $V_{Li}$ , rendering a round-trip efficiency as high as 87%, which is much better than previous reported results. The comparable charge voltage between Pt@MCN and Pt@AB electrodes indicated the responsibility of Pt nanoparticles for the OER kinetics, while the much higher discharge voltage of the Pt@MCN electrode than both Pt@AB and MCN electrodes indicated a synergistic effect caused by Pt and

MCN for the ORR kinetics. It is assumed that the combination of different catalysts would provide an effective way to improve the electrochemical performance of the lithium-air battery.

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