

Inward growth of superthin TiC skin on carbon nanotube framework as stable cathode support for Li–O₂ batteries

Chu-Shu Yang^{a,b,*}, Zhuang Sun^a, Zhonghui Cui^a, Fang-Ling Jianga^a, Jun-Wen Deng^a,
Tao Zhang^{a,b,*}

^a The State Key Lab of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai, 200050, PR China

^b Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing, 100049, PR China

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ABSTRACT

The rational design and synthetic route to fabricate stable air cathode supports, which combine high electron conductivity and desirable superoxide anion radical species ($O_2^{\cdot-}$)-against stability, remain critical but still challenging for sustainable Li–O₂ batteries. Herein, a method of inward vapor-solid growth is proposed to prepare superthin TiC skin on multi-walled carbon nanotubes framework (MWNTs) as stable support (TiC/MWNTs) for air cathodes. By adjusting reaction temperature and time, the sp²-hybrid carbon walls of MWNTs are transformed into dense TiC skins layer by layer from outside to inside. The thickness of the transformed TiC skin can be controlled at a superthin nanosized magnitude of 3 nm. Benefiting from the seamless TiC surface layer, the TiC/MWNTs possesses both the advantages of MWNTs framework (light mass and high electronic conductivity) and TiC skin (excellent $O_2^{\cdot-}$ -against stability). Besides, by loading the catalyst of Ru nanoparticles on the obtained TiC/MWNTs support, the Li–O₂ battery exhibits long-term cyclability (90 cycles) with little by-products (Li₂CO₃). The inward growth method is demonstrated to be also effective for graphene sheets and the conventional carbon blacks of Ketjenblack (KB). This achievement provides a new approach for surface enhancement of carbon electrodes from universal electrolyte corrosion problems.

1. Introduction

As the market for electrifying transportation and portable electronic devices grows quickly, energy storage systems with high energy density are attracting more and more attention than that at any time in the past. The Li–O₂ battery is promising to be an ultimate energy storage device because of its high theoretical specific energy, which is much higher than that of the state-of-art Li-ion battery. However, its realization is being hindered by some major challenges such as low Coulombic efficiency, poor cycle life, and significant overpotential. Tremendous efforts have been devoted to solving these problems [1–4]. And it has been revealed that such issues are mainly determined by the cathode materials [5]. Carbon materials, characteristics of high electrical conductivity, light-weight, and wide surface area, have been the common choices for cathodes. Despite all the attractive features, recent studies have reported that carbon exhibits thorny problems when used in Li–O₂ batteries [6–11]. Carbon is preferentially attacked by the reduced oxygen species

generated during the discharge process, and produces irreversible side-products of Li₂CO₃, lithium carboxylates, etc., owing to the highly exothermic reactions. These by-products lead to electrode passivation, taking major responsibility for severe polarization, capacity fading on cycling and premature battery death.

Considering these matters, a non-carbon-based oxygen electrode is a competitive alternative. Along with this idea, some metal oxides (Co₃O₄, Ti₄O₇, RuO₂) [12–14], precious metals (Au, Ru) [15,16], and carbides (TiC, MoC, B₄C) [17–19] have been extensively studied. However, a suitable cathode should not only be chemically and electrochemically stable but also featured with high electrical conductivity and relatively low density. If so, adopting a single component can hardly meet the stringent requirements. Recently, it has been reported that carbon substrates coated with carbon-free layers have shown more stable cyclic performances as air-cathode supports than bare carbon. Unfortunately, the deposition processes always need sophisticated equipment, such as ALD [20,21], and the “outward deposition” can hardly define or reduce

* Corresponding author. State Key Lab of High Performance Ceramics and Superfine microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai, 200050, PR China.

E-mail address: taozhang@mail.sic.ac.cn (T. Zhang).

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the thickness of coating layers, making an uncontrollable proportion of noncarbon in the carbon-based oxygen-cathodes. Adding insult to injury, the coating layer is just physically combined with the base materials, and Li_2O_2 discharge products can form at the interface between the wall of MWNTs and the coating layer, leading to the detachment of the coating film from the MWNTs [20]. Therefore, concerning the carbon/noncarbon oxygen-cathodes, there has been no significant breakthrough in the application of Li–O₂ batteries.

In this work, we employ a method of inward vapor phase growth to transform the intrinsic carbon wall of MWNTs into TiC skin by “layer to layer” and “outside to inside”. The thickness of TiC skin can be controlled easily in a magnitude of several nanometers via adjusting the reaction time and temperature. The TiC/MWNTs composite merits the advantages of both the carbon framework (light mass and high conductivity) and the TiC surface skin (chemical stability). Furthermore, Ru nanoparticles were decorated on the composite surface, which functions as the active catalyst for both oxygen reduction reaction (ORR) on discharge and oxygen evolution reaction (OER) on charge [16,22,23].

2. Experimental section

2.1. Preparation of TiC/MWNTs and TiC/MWNTs-Ru followed by assembling of integrated Li–O₂ batteries

Multiwalled carbon nanotubes (18 mg) and iodine (45 mg) were placed in one end of a quartz tube (20 cm length, 12 mm od, 10 mm id). The quartz tube was necking down in the middle position to place a titanium metal plate (240 mg, 9 mm diameter). Then the quartz tube was evacuated (6×10^{-4} Pa) and flame sealed by a Partulab device (MRVS-1002) at the titanium metal end. The quartz tube was placed into a tube furnace and the samples were then reacted under the following conditions: sample I, 560 °C (40 h); sample II, 560 °C (20 h) and 650 °C (20 h); sample III, 560 °C (10 h), 650 °C (10 h), 750 °C (10 h) and 790 °C (10 h).

Ru nanoparticles were prepared in ethylene glycol (EG) solution. 1 mg of Ru in RuCl_3 and 9 mg TiC/MWNTs were dissolved in EG solution and its pH was adjusted to 13 with 0.1 M NaOH. The solution was then heated to 160 °C for 3 h with flowing N₂. After cooling down, the obtained suspension was adjusted to pH 3 using 0.1 M HCl and then stirred for 12 h. The final product of TiC/MWNTs-Ru was centrifuged, washed with deionized water until the pH of the solution reached approximately 7, and freeze-dried for 24 h.

The TiC/MWNTs-Ru products were mixed with PTFE in a mass ratio of 9:1 in isopropanol and ultrasonically dispersed for 30 min. After being ground for 1 h in an agate mortar, the ink was then coated on the nickel foam (9 mm) and dried in a vacuum oven at 80 °C for 12 h. The loading area of each cathode was ranged from 0.385 to 0.5 cm² (7–8 mm in diameter), and the mass density of active materials was about 0.5 mg cm⁻² per electrode. And then battery assembling processes were carried out in an argon-filled glovebox. CR2032-type coin cells with holes for O₂ access were used as holders. Li metal (9 mm in diameter, 0.2 mm in thickness) was used as the anode. 0.5 mol L⁻¹ LiClO₄ in a DMSO solution was used as the electrolyte, immersing in a Watman GF/C glass fiber separator. After assembling, the batteries were transferred into an oxygen-filled high-integrity glovebox for electrochemical measurements.

2.2. Characterization

X-ray powder diffraction (Bruker D8 ADVANCE) was used to analyze the composite materials TiC/MWNTs and the discharge products of Li–O₂ batteries. To detect the by-products during battery cycles, the TiC/MWNTs-Ru and MWNTs-Ru cathodes after the 20th discharge and charge were washed by glycol dimethyl ether, dried and detected directly with ATR module FTIR (Bruker Tensor 27) from 2200 to 800 cm⁻¹ with a resolution of 2 cm⁻¹. Besides, the MWNTs, TiC/MWNTs, and TiC/MWNTs-Ru were observed by JEOL JSM-2100F for micrograph observation and EDS-mapping analysis. The X-ray photoemission spectroscopy

(XPS) data of TiC/MWNTs and MWNTs-Ru were obtained through an X-ray photoelectron spectrometer (Thermo Fisher ESCA1AB 250). Spherical aberration corrected high-resolution transmission electron microscopy (Cs-corrected HRTEM) characterization and EDS line scan were performed on a Hitachi HF5000. Inductively Coupled Plasma Mass Spectrometer (ICP-MS) was applied by a iCAP RQ. The weight loss of MWNTs and three samples were measured by thermogravimetric analysis (TGA, NETZSCH STA449C) in air. To collect the gas evolution data (DEMS), the batteries with TiC/MWNTs-Ru and MWNTs-Ru cathode were discharged to 0.35 mAh at 200 mA g⁻¹ at first. After that, the batteries were put in argon flow to get a stable baseline and recharged back along with the collecting of gas signals.

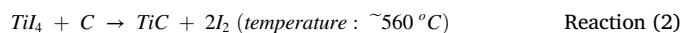
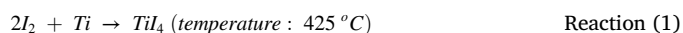
2.3. Electrochemical analysis

The cycling tests of Li–O₂ batteries were galvanostatically performed at a specific current of 250 mA g⁻¹ using a Land charge/discharge machine (Wuhan LAND Electronics Co., Ltd.). All the tests of Li–O₂ batteries were carried out in the O₂-tight glass chamber with an initial pressure of 1 atm.

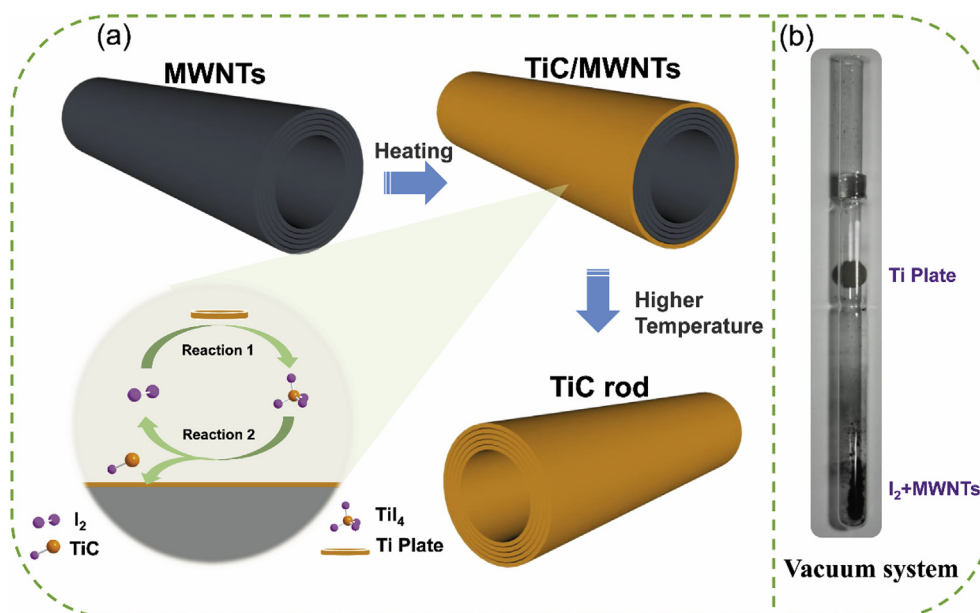
The linear sweep voltammetry (LSV, Autolab) were measured at a scan rate of 0.5 mV s⁻¹ for the Li–O₂ batteries with the cathode of TiC/MWNTs-Ru and TiC/MWNTs. And electrochemical impedance spectra (EIS, Autolab instrument) were tested with an amplitude of 10 mV in a frequency range from 1.0 MHz to 1.0 Hz.

3. Results and discussion

The synthesis schematic diagram of the TiC/MWNTs composite is shown in Scheme 1. MWNTs, iodine, and titanium sheet were placed in a quartz tube that was evacuated (6×10^{-4} Pa) and then flame sealed. Heating the quartz tube in the tube furnace, the iodine will sublime and react with the titanium to form TiI₄, which has a relatively low boiling point of 425 °C. And then the TiI₄ vapor is going to react with the carbon wall of MWNTs from outside to inside, releasing iodine again. The iodine reacts with titanium again to be utilized repeatedly. The whole reaction equations are shown as follows [24,25]:



As a result, the MWNTs will be transformed into TiC rod “layer by layer” via the “outside to inside” reaction. By adjusting the reaction conditions, it is feasible to control the thickness of the TiC layer. To shed light on the formation of the TiC/MWNTs influenced by the temperatures and reaction time, samples were prepared under the following conditions: sample I, 560 °C (40 h); sample II, 560 °C (20 h) and 650 °C (20 h); sample III, 560 °C (10 h), 650 °C (10 h), 750 °C (10 h) and 790 °C (10 h). Transmission electron microscopy (TEM) images were collected for pristine MWNTs and three as-prepared samples, as shown in Fig. 1a–d. These images have proved that the TiC layer was formed from MWNTs’ exterior surface and its thickness increased with the increase of reaction time and temperature. At the same time, the carbon wall of the MWNTs lessened gradually and finally, the MWNTs totally changed into TiC. Especially, the TiC layer can be controlled in a magnitude of nanometers such as sample I (~1 nm) and sample II (~3 nm). The relative content of TiC and MWNTs were then investigated by X-ray diffraction (XRD) in Fig. 1e. Corresponding to the TEM data, the sample I showed strong carbon peak and weak TiC peak, while the TiC peaks of the sample II became stronger along with the weaker carbon peak. It means that more portion of carbon has been converted to TiC at a high temperature. Furthermore, almost all MWNTs were transformed to TiC as only TiC peaks existed in the XRD pattern of the sample III. Moreover, EDS line scan (Figure S1) revealed the core-shell structure of TiC/MWNTs with the carbon atoms confined in the core and the Ti atoms located on the outer



Scheme 1. Schematic illustration of synthesis of TiC/MWNTs and vacuum system: (a) The surface layer of MWNTs transforming to the TiC by heating, and the whole MWNTs transforming to TiC rod with the improving of reaction time and temperature. (b) Vacuum flame sealing the quartz tube containing the MWNTs, I₂, and Ti plate.

shell. Besides, EDS line scan showed the existence of a small number of oxygen atoms appeared along with the Ti atoms, which may be attributed to the TiO₂. To identify the proportion of carbon in the composite, TG curves of 100 µg MWNTs, sample I, sample II and sample III were heated at 5 °C min⁻¹ in air are shown in Fig. 1f. The carbon contents in these three samples were calculated as 93%, 25%, and 2%, respectively. The oxidation of the TiC surface layer leads to the mass increase of sample II and sample III. To avoid the influence caused by the transition from TiC to TiO₂, ICP-MS measurements were performed to accurately obtain the titanium content for three TiC/MWNTs samples, including sample I, sample II, and sample III. As shown in Table S1, the titanium content for the samples I, II, and III is 8.4%, 54.4%, and 78%, respectively. According to these results, the carbon content of the three samples can be calculated as 89.5%, 32%, and 2.4%, respectively, which is basically consistent with the previous TG results. Interestingly, XPS data shows that the surface of the TiC/MWNTs contains not only TiC (454.7 eV and 460.7 eV) but also significant proportions of TiO₂ (458.5 eV and 464.3 eV), as demonstrated in Fig. 1g [17]. TEM image also confirms this result, as shown in Fig. 1h, the surface of the TiC, the d-spacing of which is 0.21 nm, contains significant proportions of TiO₂ with the d-spacing of 0.23 nm [26–28]. Therefore, it can be inferred that the surficial TiO₂ may be naturally formed by the oxidation of TiC, which has also been reported by Bruce et al. [17]. Thus, the composite can still be denied as TiC/MWNTs despite the partial oxidation of TiC on the surface.

To investigate the stability of the TiC/MWNTs for the superoxide, the TiC/MWNTs and the pristine MWNTs were put into the metastable superoxide solution for 30 min [29], and then Fourier Transform Infrared (FTIR) spectra were collected as shown in Fig. 2a. The pristine MWNTs showed much stronger peaks of carbonate after immersion, while the TiC/MWNTs showed significantly weaker peaks. Thus, it can be inferred that the TiC surface layer is more stable with the superoxide species than the carbon wall of the MWNTs. Furthermore, if the TiC/MWNTs was heated at 350 °C for 30 min, the TiC layer will be converted into TiO₂ completely (Figure S2a) [30]. However, the carbonate peaks in the XRD pattern of the TiO₂/MWNTs were almost the same as that of TiC/MWNTs after immersion, while the electrochemical performance became worse, as shown in Figure S2b [31]. This is mainly because TiO₂ lacks ORR and OER catalytic ability so that it can inhibit the electrochemical performances even with only a thin layer [32]. Nazar et al. reported that the

surface of the TiC powder can influence the electrochemical performance when used as cathode materials. The TiC-B powder with partly oxidized surfaces such as TiC, TiO_xC_y, and TiO₂ can keep the balance of stability and electronic conductivity, of note is that the TiC-B mainly exposes (200) planes [32]. While the other kind of powder TiC-A, whose surface is oxidized completely to TiO₂ layer, lacks ORR and OER catalytic ability. To distinguish the exposed planes of TiC layer outside the TiC/MWNTs, the high-resolution transmission electron microscopy (HRTEM) was used. As shown in Figure S3, the exposed planes of TiC layer in this work are determined to be (200), which is consistent with the TiC-B type. Thus, TiC/MWNTs can possess the partly oxidized surface which is demonstrated by XPS data (Fig. 1g). Benefiting from the hybrid surfaces, the TiC layer can protect the carbon substrate from attacks of O₂²⁻ during cycling. To further confirm the stability of TiC/MWNTs and MWNTs, cathodes after different cycles were tested by XPS as shown in Figure S4. After the first cycle of the MWNTs cathode, an obvious peak appeared at around 289.5 eV which can be ascribed to Li₂CO₃ [33]. And the Li₂CO₃ peak became sharper after the 10th cycle. While weak Li₂CO₃ peaks were found on the TiC/MWNTs cathode after the 1st and 10th cycle. Thus, it can be confirmed that TiC layer with the partly oxidized surface can effectively reduce the side products which may damage the catalyst ability. Considering the safeguard effectivity of the TiC surface layer, the sample II is chosen as the next experiment sample rather than sample I in which the TiC skin is too thin to protect the MWNTs thoroughly (Fig. 1b). The TEM image of sample II with a broader view is shown in Figure S5, in which almost all of the MWNTs framework is covered by the superthin TiC skin. The discharge and charge curves of sample II and the pristine MWNTs in the first cycle were tested with a double limitation of both discharge/charge of 1000 mAh g⁻¹ and voltage of 2.3–4.0 V at 250 mA g⁻¹. The MWNTs cannot be charged back to 1000 mAh g⁻¹ when the cut-off voltage is limited at 4.0 V, which could be attributed to the formation of by-products (Figure S6a). And the cycle performance of MWNTs decayed quickly compared with the TiC/MWNTs which further proves the protective effect of TiC layer on the cathode (Fig. 2b and c). Besides, the TiC/MWNTs composed of a low density of MWNTs substrate and an atomic layer of TiC can retain higher capacity compared with pure TiC as shown in Fig. 2d. Furthermore, cyclic voltammetry (CV) was also performed to detect the OER and ORR performances of TiC/MWNTs and MWNTs. As shown in Figure S6b, on the one hand, the intensities of both

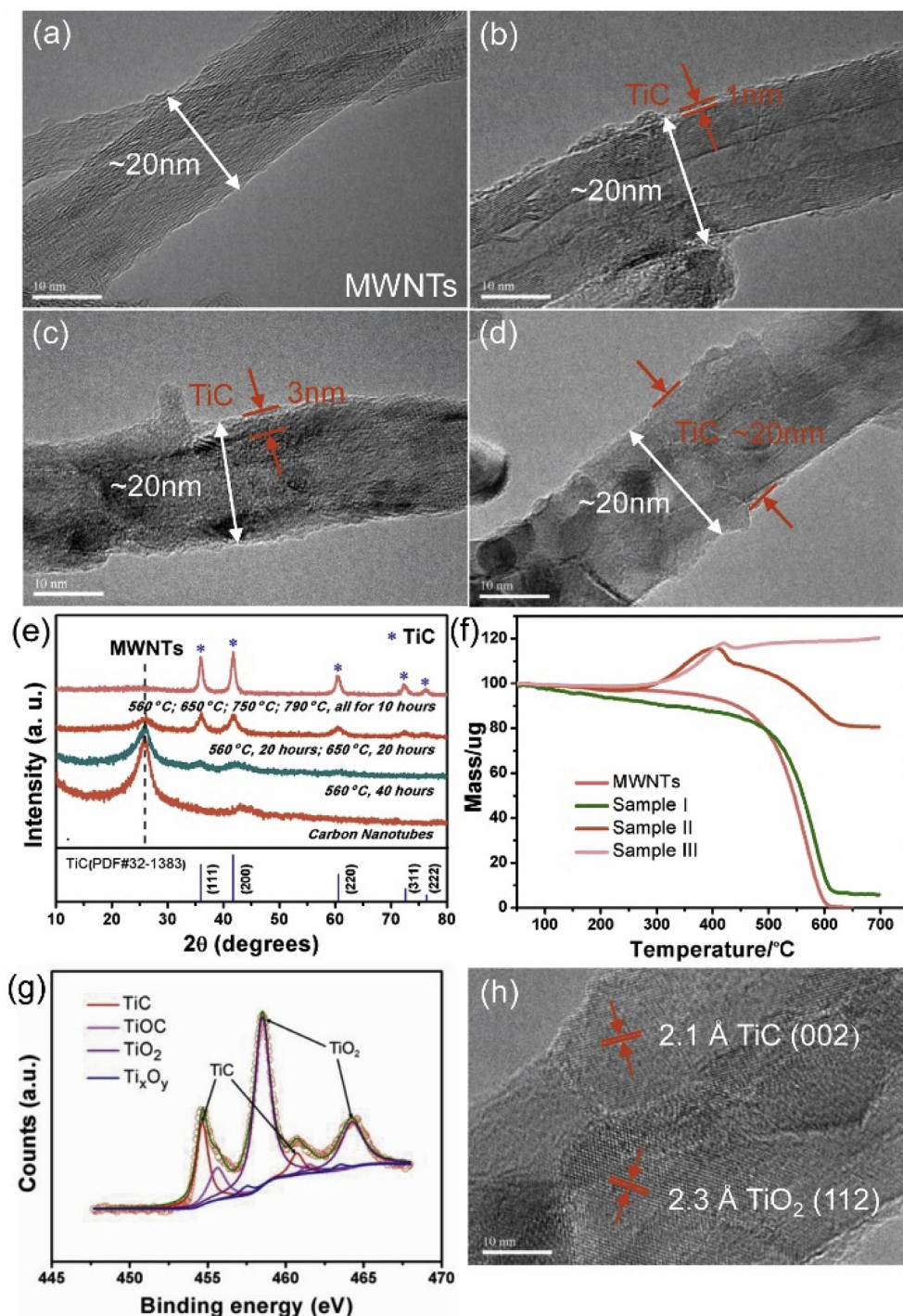


Fig. 1. TEM images of (a) MWNTs, (b) sample I, (c) sample II, and (d) sample III, (e) XRD patterns of MWNTs and three TiC/MWNTs samples prepared at three conditions, (f) Curves for the TG of 100 μg of MWNTs, sample I, sample II, and sample III heated at 5°C min^{-1} in Air, (g) XPS data of the sample II (TiC/MWNTs), (h) HRTEM of the surface of sample III.

OER and ORR peaks of TiC/MWNTs are higher than those of MWNTs; and on the other hand, the difference between redox peaks of TiC/MWNTs is smaller than that of MWNTs, verifying the better ORR and OER performances of TiC/MWNTs. Also, the discharge curves (fully to 2.3 V) of the pristine MWNTs, TiC/MWNTs (sample II) and the pure TiC nanorods are shown in Fig. 2e. MWNTs delivered the highest capacity of 3841 mAh g^{-1} than the TiC/MWNTs composite and TiC rod benefiting from the low density of carbon. Inherited this advantage, the TiC/MWNTs (sample II) has a capacity of 1800 mAh g^{-1} , which is more than three times the capacity of the pure TiC. Moreover, TiC/MWNTs

displayed a smaller impedance than TiC owing to the combination with MWNTs (Figure S7). Thus, it can be inferred that TiC/MWNTs possesses both the advantages of MWNTs and TiC. However, TiC/MWNTs is not catalytic enough to achieve multiple cycles as shown in Fig. 2b. This result confirms that the TiC/MWNTs cathode demands to composite with an active catalyst to decrease the overpotential of ORR and OER processes.

Ru metal has been reported to be an efficient catalyst for both ORR and OER on charge [16,22,23]. Herein, Ru nanoparticles were synthesized in ethylene glycol (EG) and then deposited on TiC/MWNTs.

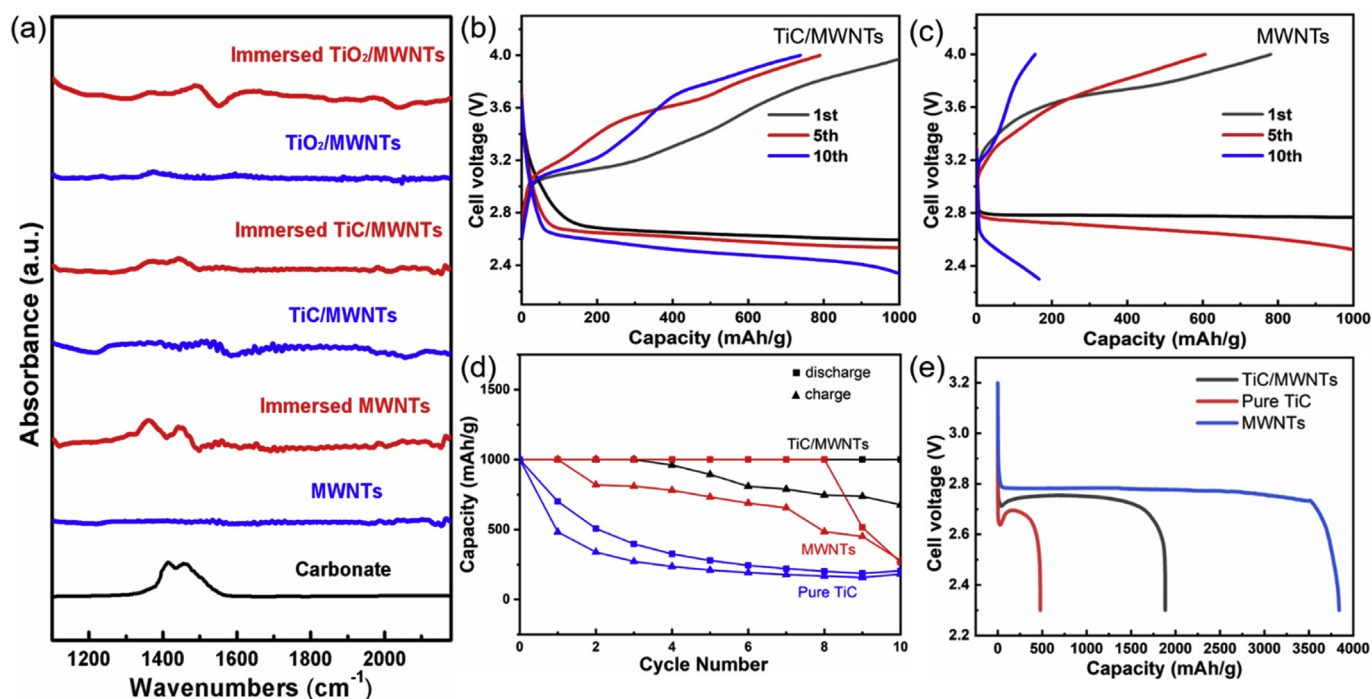


Fig. 2. (a) FTIR spectra of MWNTs, TiC/MWNTs, and TiO₂/MWNTs before and after immersed in KO₂ for 30 min, Voltage profiles of (b) TiC/MWNTs and (c) MWNTs at 250 mA g⁻¹ with the capacity restriction of 1000 mAh g⁻¹ and voltage range of 2.3–4.0 V, (d) the cycling performance of Li–O₂ battery with cathode of TiC/MWNTs, MWNTs, and pure TiC (250 mA g⁻¹), (e) Complete discharge to 2.3 V curve of TiC/MWNTs (sample II), MWNTs, and pure TiC.

As shown in Fig. 3a, the nanoparticles with an average diameter of 3 nm are distributed uniformly on the surface of TiC/MWNTs uniformly. The *d*-spacing of the attached particle is ~0.21 nm, which is corresponding to the facet of Ru (002) [16]. Meanwhile, the XPS data in Figure S8 also proves the existence of Ru. The EDS-mapping analysis of TiC/MWNTs-Ru in Fig. 3b–e exhibited the existence of carbon (C), titanium (Ti), oxygen (O), and ruthenium (Ru). The fine distribution of Ru on the TiC/MWNTs is consistent with the above-mentioned TEM results.

The TiC/MWNTs-Ru was then used as the oxygen cathode (support with catalyst) of Li–O₂ batteries. Figure S9 shows the first discharge-charge curves of the Li–O₂ batteries with the TiC/MWNTs and TiC/MWNTs-Ru respectively. The Li–O₂ battery with the TiC/MWNTs-Ru cathode exhibited a relatively lower mid-capacity overpotential of 0.49 V (the overpotential at middle capacity) than that with TiC/MWNTs cathode (0.79 V). This result suggests that the anchored Ru indeed improves both the OER and ORR performances. To investigate the effect of the TiC skin on the cycling performance, the batteries were further tested under the galvanostatic mode with a double limitation of both discharge/charge capacity of 1000 mAh g⁻¹ and voltage range of 2.3–4.0 V at 250 mA g⁻¹, depending on which parameter reaches firstly. As shown in Fig. 3f and g, the Li–O₂ battery with the TiC/MWNTs-Ru cathode maintained its major performance properties, such as capacity and mid-capacity voltage profiles, during 90 cycles. In stark contrast, the battery with the MWNTs-Ru cathode exhibited much worse reversibility. In detail, the discharge capacity of the former retained 1000 mAh g⁻¹ at the 90th cycles and the charge capacity retained 940 mAh g⁻¹ as shown in Fig. 3i. However, a sharp increment of polarization voltage appeared after 60 cycles for the battery with the MWNTs-Ru cathode, and the charge capacity dropped fast and finally can only retain 363 mAh g⁻¹, as shown in Fig. 3j. It is mainly attributed to the accumulation of side reaction products including Li₂CO₃ (derived from carbon and electrolyte) and Li carboxylates (derived from the electrolyte), which are decomposed incompletely under 4.0 V [8].

Furthermore, the CVs of TiC/MWNTs-Ru and MWNTs-Ru at a scan rate of 0.5 mV s⁻¹ from 2.3 to 4 V are presented in Figure S10. The OER and ORR current intensities of MWNTs-Ru tended to decrease which may

be induced by the decomposition of the cathode. The OER and ORR currents of TiC/MWNTs-Ru are more stable than those of MWNTs-Ru. The nanoscale TiC layer of TiC/MWNTs-Ru prevents the inner MWNTs from contacting with both the Li₂O₂ product and electrolyte, which can reduce the accumulation of side reaction products. The XRD results in Figure S11 confirm the existence of Li₂O₂ at the discharge state of TiC/MWNTs-Ru in DMSO, and the peak of Li₂O₂ disappeared after the recharging. It proves the good reversibility of battery with TiC/MWNTs-Ru. To further confirm the discharge product of batteries with TiC/MWNTs-Ru, in situ XPS was used to test the Li–O₂ batteries with TiC/MWNTs-Ru after the 1st, 20th, and 50th discharge. As shown in Figure S12a, c and e, the Li 1s peaks at 54.5 eV and 55.4 eV are ascribed to Li₂O₂ and Li₂CO₃ respectively [13]. It is obvious that the discharge products are mainly Li₂O₂, only a small amount of side products appeared (mainly Li₂CO₃). As the number of cycles increased, the contents of Li₂CO₃ increased gradually which may be ascribed to the degradation of electrolyte [34]. Furthermore, scanning electron microscope (SEM) was applied to directly observe the morphologies of discharge products. As shown in Figures S12b, d and f, disc-like Li₂O₂ particles around 300 nm are the main discharge products. However, some side products are also found after 20 and 50 cycles, which may be from the degradation of electrolyte or the by-products residuals during cycles. But for the MWNT-Ru cathode (Figure S13) after 1st discharge, the formed Li₂O₂ may react with the carbon substrate and cannot remain a regular shape. It is worth noting that the stability of the DMSO electrolyte can also be influenced by the cathode. It has been reported that carbon materials tend to accelerate the decomposition of electrolytes [8,35]. As shown in the linear sweep voltammetry (LSV) (Fig. 3h), the electrolyte in the TiC/MWNTs-Ru Li–O₂ battery exhibited an oxidation stability limit of 4 V, which is 0.15 V higher than that of Li–O₂ battery with MWNTs-Ru cathode. This result confirms that TiC/MWNTs could restrain the decomposition of electrolyte relatively compared with bare MWNTs.

Further evidence about the stability of TiC/MWNTs cathode has been shown in FTIR spectra. The samples were collected from TiC/MWNTs-Ru and MWNTs-Ru after 20th in Fig. 3k. The transmission peaks at around 880 cm⁻¹ and 1500 cm⁻¹ are the signatures of Li₂CO₃ which can be

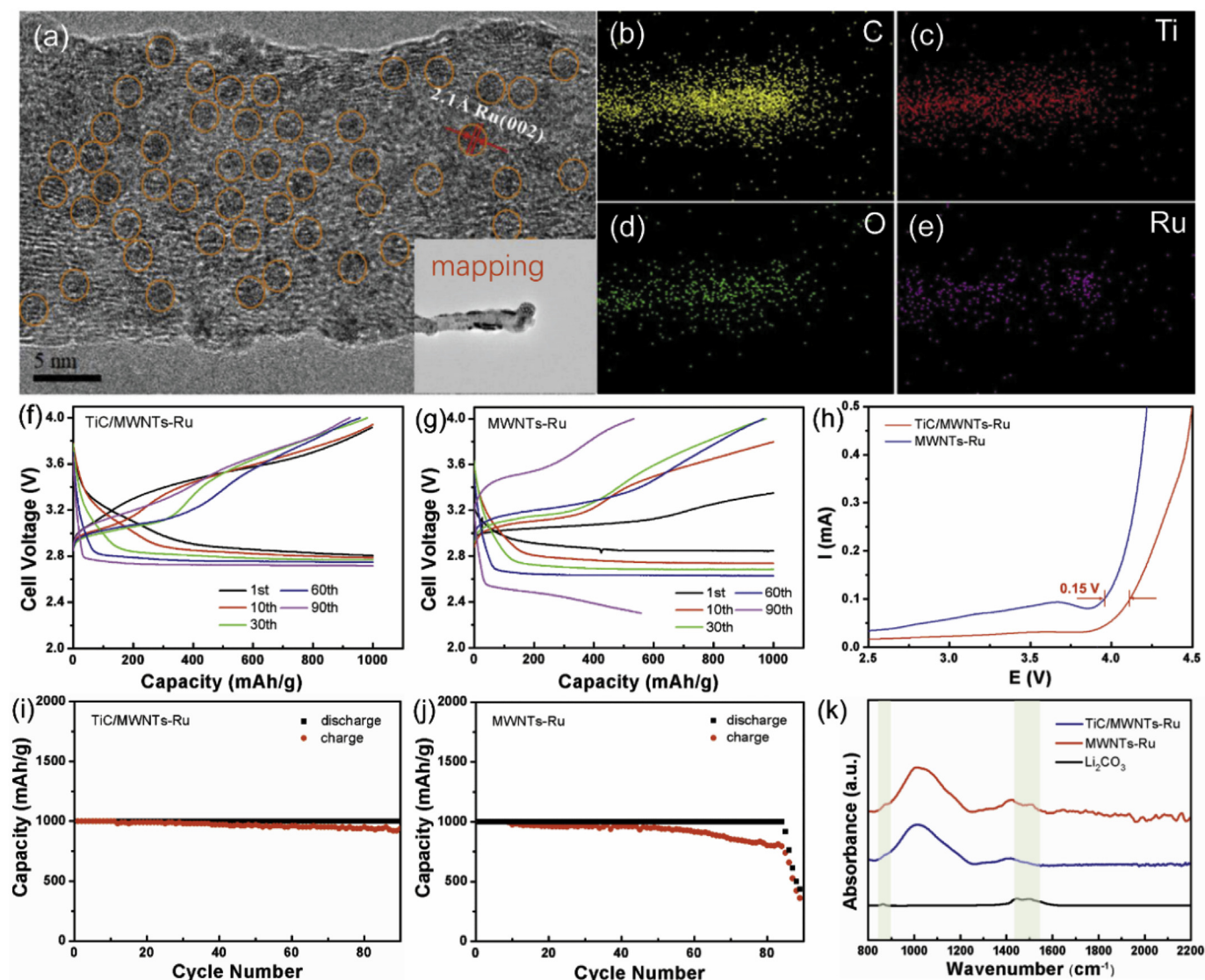


Fig. 3. (a) TEM image of the TiC/MWNTs-Ru, EDS-mapping images of TiC/MWNTs-Ru: (b) carbon (C, yellow), (c) titanium (Ti, red), (d) oxygen (O, green), and (e) ruthenium (Ru, purple). The voltage profiles of Li–O₂ battery with cathode of (f) TiC/MWNTs-Ru and (g) MWNTs-Ru at a current density of 250 mA g^{−1}, (h) LSV curves of the batteries with TiC/MWNTs-Ru or MWNTs-Ru cathode, The cycling performance of Li–O₂ battery with cathode of (i) TiC/MWNTs-Ru and (j) MWNTs-Ru (250 mA g^{−1}) (k) FTIR spectra of TiC/MWNTs-Ru and MWNTs-Ru cathode after 20 cycles at charge state.

found obviously in the MWNTs-Ru cathode [36–38]. The formation of Li₂CO₃ is mainly derived from MWNTs or the electrolyte by direct contacting the reduced oxygen species (especially Li₂O₂). By the rational design and precise control of the carbon/noncarbon composite, the intensity of Li₂CO₃ peaks in TiC/MWNTs-Ru was much weaker than that of MWNTs-Ru, indicating that the MWNTs are fully protected by the TiC layer from the reactive intermediates and electrolyte attacks. Thus, TiC/MWNTs-Ru can be more integrated with little loss of cathode materials. As shown in Figure S14, the MWNTs-Ru was significantly broken after 50 cycles under the continuous attack of superoxide and reaction with electrolyte. While TiC/MWNTs-Ru appeared flatter than MWNTs with the protection of TiC skin. Besides, in situ differential electrochemical mass spectrometry (i-DEMS) was applied to detect the composition of the gas evolution in the charging process of the first cycle [39,40]. Li–O₂ batteries with TiC/MWNTs-Ru and MWNTs-Ru were first discharged to 0.35 mAh at 200 mA g^{−1} and then recharged back as shown in Fig. 4a and b. The results of gas evolution are shown in Fig. 4c and d. It is found that the CO₂ evolution from TiC/MWNTs-Ru cathode was much lower than that of MWNTs-Ru cathode, implying that Li–O₂ battery with TiC/MWNTs-Ru cathode generated little by-product such as carbonates

which was responsible for the little CO₂ evolution. And it is worth noting that there is little O₂ evolved proportionally to the CO₂ evolution at the end of the charging process, which may come from the decomposition of by-products.

Furthermore, the controllable route of inward vapor phase growth is not just suitable for the MWNTs, other carbon materials like graphene and even the common carbon materials Ketjen black (KB) can be partially transformed to TiC as shown in Figure S15. That means the controllable method of inward vapor phase growth is universal for the combination of carbon materials and non-carbon materials, which has a great prospect in the practical application of lithium-air batteries [41,42].

4. Conclusion

In conclusion, superthin TiC skin on MWNTs framework as stable cathode support has been fabricated by a “layer by layer” and “outside to inside” inward vapor-phase process. The thickness and proportion of the TiC layer outer of the carbon substrate can be controlled precisely. Benefiting from the nanosized dense TiC layer, TiC/MWNTs possess both the advantages of MWNTs (light mass and high electronic conductivity)

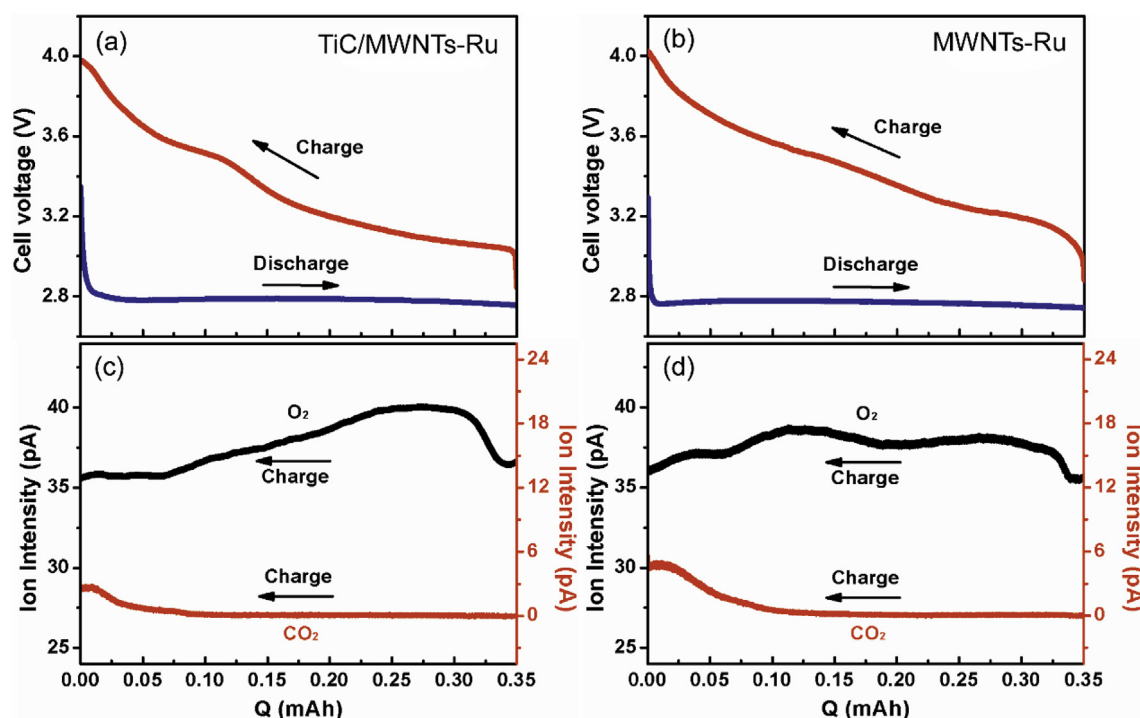


Fig. 4. Galvanostatic discharge and charge curves of Li–O₂ battery at 200 mA g^{−1} with cathode of (a) TiC/MWNTs-Ru and (b) MWNTs-Ru and the corresponding gas evolutions (c) and (d) from DEMS measurements.

and TiC (excellent chemical stability). The rationally designed TiC/MWNTs show superior stability towards superoxide from the chemical and electrochemical tests. Besides, by loading Ru nanoparticles on the designed TiC/MWNTs, Li–O₂ batteries with TiC/MWNTs-Ru cathode obtain long-term cyclability (90 cycles) with little by-products (Li₂CO₃). Furthermore, the synthesis route is not only effective for MWNTs but also useful for graphene, KB and so on. It is an efficient method for the combination of advantages of carbon materials and non-carbon superthin surface coating layer to resist the universal carbon corrosion problems. We believe that this combination approach is the right way to improve the cathode stability of Li–O₂ and Li-air batteries. Hopefully, it is also suitable for the precise surface enhancement of carbon materials in the fields of fuel cells, solar cells, electrocatalysis and so on.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Chu-Shu Yang: Investigation, Writing - original draft. **Zhuang Sun:** Validation, Investigation. **Zhonghui Cui:** Formal analysis, Funding acquisition. **Fang-Ling Jianga:** Formal analysis. **Jun-Wen Deng:** Resources. **Tao Zhang:** Supervision, Conceptualization, Formal analysis, Funding acquisition, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.ensm.2020.04.018>.

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