A facile method to fabricate N-doped graphene-like carbon as efficient electrocatalyst using spent montmorillonite

Shanshan Yang^a, Pingxiao Wu^{a,b,c,d*}, Liya Chen^a, Ligui Li^a, Zhujiang Huang^e, Shuai Liu^a, Liping Li^a,

a College of Environment and Energy, South China University of Technology, Guangzhou 510006, P.R. China

b The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, Guangzhou 510006, P.R. China

c Guangdong Provincial Engineering and Technology Research Center for Environmental Risk Prevention and Emergency Disposal, South China University of Technology, Guangzhou Higher Education Mega Centre, Guangzhou 510006, PR China

d Guangdong Environmental Protection Key Laboratory of Solid Waste Treatment and Recycling, Guangzhou 510006, China

e College of Natural Resources and Environment, South China Agricultural University,

Guangzhou 510642, P.R. China

*Corresponding author: Tel.: +86-20-39380538; Fax: +86-20-39383725.

E-mail: pppxwu@scut.edu.cn (P.X. Wu).

Abstract

Montmorillonite (Mt), as an efficient adsorbent, has been widely applied in the treatment of wastewater. However, it is important to develop appropriate disposal

methods, which are currently lacking for ~~discarded~~ spent Mt after adsorption. We utilized Mt after adsorption of Tetracyclines (TC) as carbon source to obtain a by-product, N-doped graphene-like carbon-based electrocatalysts (TC-C), by a facile and low cost pyrolysis strategy. Physicochemical and electrochemical characterization of TC-C indicated that the resultant TC-C was made up of many ultrathin nanosheets, which resembled the morphology of graphene, and it had a large Brunauer-Emmett-Teller surface area with narrow slit-like pores. Nitrogen doping was evaluated through X-ray photoelectro-spectra measurements and four nitrogen-bonding configurations were identified and quantified, including pyridinic N, pyrrolic N, graphitic N and pyridinic N⁺-O⁻. Electrochemical studies showed that TC-C exhibited high catalytic activity for the oxygen reduction reaction (ORR) in alkaline medium with outstanding methanol tolerance compared to the commercial Pt/C catalysts. Furthermore, the effect of the adsorbed amount of TC on the ORR activity of TC-C was slight and the pyrolysis temperature of 700 °C was demonstrated to be the optimal temperature for the pyrolysis process in the recycling of spent Mt.

Keywords: Graphene-like carbon material; Nitrogen doping; Electrocatalyst; Spent Mt; Oxygen reduction reaction

1 Introduction

Clay minerals, including montmorillonite (Mt), have drawn much attention as functional nanomaterial due to their particular advantages such as chemical and mechanical stability, large specific surface area and high cation exchange capacity (CEC) (Hussin et al. 2011). Mt, a 2:1 layered silicate clay mineral, is composed of one

octahedral sheet sandwiched by two tetrahedral sheets and its layer includes negative charge, which is balanced by inorganic cations such as Na^+ and Ca^{2+} . Moreover, these inorganic cations are exchangeable, making Mt as an efficient adsorbent for various cationic contaminants (Gupta et al. 2009). Numerous studies have reported that Mt can be used as efficient adsorbent to remove Tetracyclines (TC) from wastewater or serve as an important pool for TC in natural soil environment (Zhao et al. 2012). In addition, the inorganic cations in the interlayer of Mt were exchanged by these molecules according to the increasing basal spacing of Mt by about 0.5 nm ~1 nm (Chang et al. 2009). Meanwhile, for template carbonization technique, Mt has been extensively employed as an inorganic template to obtain carbon-clay nanocomposites after pyrolysis of organic molecular associated to Mt. Some authors have also reported to prepare graphene-like materials by an eco-friendly method, which used resources supported on Mt as precursor without the presence of reducing agents (Gómez-Avilés et al. 2010; Ruiz-Hitzky et al. 2011). In this process, the adsorbed organic compounds are considered to be carbon sources and can be transformed into carbon materials after pyrolysis under inert atmosphere with the support of inorganic template. It was noted that the 2D graphene-like nanomaterials can be obtained by liberating Mt layers followed acid washing (Wang et al. 2006). The resultant graphene-like nanomaterials showed special physicochemical properties and utilization prospect, such as hydrogen storage (Ruiz-Garcia et al. 2013), anode materials in Li-ion batteries (Xu et al. 2013), cathode catalysts for fuel cell oxygen reduction reaction (ORR) (Chen et al. 2016; Qazzazie et al. 2015; Zhu et al. 2015) and so on. For instance, C. Ruiz-Garcia

and his co-worker reported that clay-graphene nanomaterials can be obtained by a green way using caramel from sucrose and two types of natural clay (montmorillonite and sepiolite) as precursors, and they are potentially useful for H₂ storage at room temperature(Ruiz-Garcia et al. 2013).

In order to deal with the ever increasing energy and environmental problems, fuel cells, as a clean and high-efficiency device, have drawn increasing interests nowadays(Sun et al. 2011). At the same time, the preparation of advanced materials for fuel cells has become an urgent research topic. Pt-based materials are regarded as commercial ORR catalysts because of the high electrocatalytic activity. However, the intrinsic drawbacks of Pt-based materials include, high cost, inferior long term stability and methanol fuel crossover effect, hence finding low-cost, efficient and stable alternative materials are of significance to satisfy the wide-spread commercialization of fuel cells(Aghabarari et al. 2013;Song et al. 2014;Wood et al. 2014). In particular, the development of nitrogen-doped carbon materials, including (carbon nanotube(Ratso et al. 2014), ordered mesoporous graphitic arrays(Liu et al. 2010) and graphene(Dou et al. 2014;Wang et al. 2014), which present excellent electrocatalytic activities as well as low cost, good durability and environmental friendliness, has been the focus of recent research (Yang et al. 2013). Asefa et al. reported the successful fabrication of N-doped porous carbon by polymerizing polyamine in situ with the pores of SBA-15 mesoporous silica, and they demonstrated that N-doped porous carbon exhibited increased current density and decreased overpotential compared to Pt/C catalysts, which was ascribed to the doping of

nitrogen atoms(Silva et al. 2013). Pan et al. used the porous sucrose- derived sphere, prepared by hydrothermal treatment of mixture consisting of sucrose and silica colloids, as precursor to fabricate N-doped graphene (NG) based on the thermal condensation of dicyandiamide, and the electrochemical measurements indicated that the NG could serve as an efficient ORR electrocatalyst in alkaline solution(Pan et al. 2015). However, to the best of our knowledge, the preparation of N-doped carbon materials usually required addition of carbon and nitrogen source as precursor, which was not beneficial for cost reduction and scale-up production(Peera et al. 2015;Rybarczyk et al. 2015). From our viewpoint, spent Mt, which had used as an ~~adsorbent~~ adsorbent for the adsorption and removal of organic contaminants such as TC from wastewater, could be recycled to make N-doped carbon materials. In addition, TC contain heteroatoms of nitrogen, which may be incorporated into the obtained carbon materials and then influence their microstructure and properties. Furthermore, the utilization of environmental waste products as precursor to fabricate functionalized materials for the production of energy can simultaneously resolve the environmental problems and energy shortage. Herein, according to this method, we could not only dispose spent Mt to avoid secondary pollution, but also obtain a kind of by-product, N-doped carbon materials, which exhibit superior structure and properties.

In this study, we utilized spent Mt, which had adsorbed TC, as precursor to fabricate N-doped graphene-like carbon-based catalysts followed by pyrolysis under N₂ atmosphere and acid washing with HF and HCl, respectively. The physicochemical

characterization of the obtained carbon-based catalysts were characterized by power X-ray diffraction (XRD), Raman spectra, field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray photoelectro-spectra (XPS) and Nitrogen adsorption-desorption experiments. The results demonstrated that carbon-based catalysts with wrinkled graphene features were successfully doped with nitrogen atoms and exhibited a high specific surface area. Electrochemical studies were performed to evaluate the activity of carbon-based catalysts towards ORR, and the results showed that the N-doped graphene-like carbon nanomaterials presented suboptimal catalytic activity and high stability for ORR, as compared to the commercial 20 wt% Pt/C catalyst. In addition, we investigated the amount of adsorbed TCs TC and the pyrolysis temperature on ORR activity of catalysts. This provided new insights into the reuse of spent Mt and new method for synthesis of incorporation of heteroatom into graphene-like carbon-based catalysts for the efficient reduction of O₂ in fuel cells.

2 Material and Methods

2.1 Materials

Mt used in this study were purchased from Nanhai, Guangdong province, China. It has a cation exchange capacity (CEC) of 0.78 meq·g⁻¹ and a specific surface area of 71 m²·g⁻¹. The chemical composition of Mt are 50.8%, 32.4%, 6.75%, 1.86%, 1.7%, 0.09%, 0.72% and 2.07% for O, Si, Al, Mg, Ca, K, Na and Fe, respectively, which was determined by X-ray fluorescence. TC (96% purity) was purchased from Aladdin Chemistry Co. Ltd., and was stored at -20°C. HF (40 wt%) and HCl (37 wt%)

were supplied by Guangzhou Chemical Reagent Factory (China). All the chemicals were used without further purification.

2.2 Sample preparation

2.2.1 Preparation of Mt-TC nanocomposite as the spent Mt

Adsorption experiments were carried out to obtain the spent Mt. A typical procedure is as showed in Surporting Information. The obtained Mt-TC nanocomposite with different TC loading amount were dried in vacuum oven at 233 K until constant weight and were denoted as Mt-TC-m, where m-the initial concentration of TC solution.

2.2.2 Preparation of graphene-like carbon materials using the spent Mt

The obtained precursors (Mt-TC-m) were placed in a quartz boat and then were pyrolyzed at different temperature from 600 to 900°C for 3h at a rate of 5°C·min⁻¹ under N₂ flow, followed by cooling down to room temperature. The pyrolysis process was to carbonize the adsorbed TC on Mt and the resulting carbon-Mt composites were denoted as Mt-TC-C-m-r, where r-the pyrolysis temperature. After that, the carbon-Mt composites were washed with 20 wt% HF and 18 wt% HCl for 2 h, respectively, and repeated for 3 times to liberate carbon materials from Mt absolutely, followed by filtration and drying. The resulting carbon materials were donated as TC-C-m-r.

2.3 Physicochemical characterizations of the carbon materials

XRD of samples, such as Mt, Mt-TC, Mt-TC-C and TC-C, were analyzed by a D8-ADVANCE X-ray diffractometer, operated on Cu Ka radiation ($\lambda=0.154$ nm) at 40 kV and 40 mA, with a scan step of 0.02°, a rate of 19.2 s per step and a scan range

between 2° and 70°. The Raman spectra were recorded by the Raman spectroscopy (Renishaw), using 514 nm laser. The microstructure of the samples' external surface was investigated by a field emission scanning electron microscopy (FE-SEM, Carl Zeiss, Germany) with an accelerating voltage of 20 kV. A transmission electron microscopy (TEM, JEM-3010, JEOL Ltd., Japan) with an accelerating voltage of 200 kV was used to study the structure of carbon materials, and mapping images were also taken by TEM to analyze the distribution of nitrogen atom. The XPS analyses were obtained with an X-ray photoelectron spectrometer (AES430S, ANELVA, Japan). Nitrogen adsorption-desorption experiments for surface and porosity quantification were performed with Chemisorption Surface Area Analyzer (ASAP 2010, Micromeritics, USA). The surface areas were estimated by using the Brunauer-Emmett-Teller method. Thermo-gravimetric and differential scanning calorimetry (TG-DSC) analyses were carried out by using a thermal analysis meter (STA-449F3, Netasch, Germany) under N₂ atmosphere with a heating rate of 5°C·min⁻¹ from 30 to 900°C.

2.4 Electrochemical measurements

Electrochemical measurements were performed at a computer-controlled potentiostat (CHI 660E, Shanghai Chenhua Instrument Co., China) with a three-electrode electrochemical cell using Ag/AgCl and a plat-inum foil served as reference and counter electrode, respectively. To prepare the working electrode, the glassy carbon disk (GC) was modified with carbon catalyst to form the catalysts layer. In brief, 2 mg catalyst was firstly ultrasonically dispersed in 1 mL ethanol to form

dispersion and then 10 μL Nafion emulsion was added into the dispersion. Secondly, 10 μL of this dispersion was deposited onto the surface of GC and dried at room temperature for electrochemical test. 20 wt% commercial Pt/C was deposited on the electrode under the same procedure.

Electrochemical measurements were taken to evaluate ORR activity of TC-C, including cyclic voltammograms (CV), rotating ring-disk electrode (RRDE) voltammetry and chronoamperometry recorded in 0.1M KOH solution, which was equipped with a gas flow system and purged with high purity nitrogen (N_2) or oxygen (O_2) for at least 30 min prior to each measurement at room temperature. The CV was performed from +0.2 to -1.0 V (vs Ag/AgCl) with the sweep rate of $10 \text{ mV} \cdot \text{s}^{-1}$. For rotating disk voltammetry measurements, the same amount of catalyst was loaded on a rotating ring-disk electrode. The polarization curves for ORR were recorded in the O_2 -saturated 0.1M KOH with a potential scan rate of $10 \text{ mV} \cdot \text{s}^{-1}$ at various rotation speeds from 100 to 2500 rpm. The stability test were carried out by using chronoamperometric measurements at +0.4 V and a rotation speed of 900 rpm in a 0.1 M KOH solution saturated with O_2 . All electrochemical measurements were performed at room temperature and the geometrical surface area of the electrode was used to calculate the current density.

3 Results and discussion

3.1 Physicochemical characterization of the carbon materials

The thermal and gravimetric behavior of TC and Mt-TC during pyrolysis process in N_2 atmosphere was analyzed up to 900°C . From Fig.1a, the first step with the DTG

peak indicated that TC melted at about 237.2°C and other endothermic processes took place between 200 and 400°C should be ascribed to the decomposition of TC. Noted that, one can see that Mass loss of TC was significant and continued up to 600°C in the TG curve. Within this temperature range, three obvious mass loss steps could be observed. At higher temperatures, TC were progressively pyrolyzed and transformed into a carbon material at about 600°C, when the total mass loss remained constant at approximately 60%. With respect to Mt-TC nanocomposite, DTA and TG curves (Fig.1b) showed a similar behavior except for the endothermic peak around 90°C, which was associated with the elimination of water. However, the endothermic steps of TCs TC seemed to be less clear and that might be ascribed to the dehydroxylation of Mt, which overlapped with the decomposition of TC. After the temperature rose to above 600°C, mass loss of Mt-TC became less obvious, although it still continued. Therefore, the transforming of Mt-TC nanocomposite into carbon/Mt composite may be well achieved at 600°C. As aforementioned, the pyrolysis process should involve the mass loss steps of desorption of water molecules, decomposition of TC, dehydroxylation of Mt, and slow carbonization of TC (Fig. 1b). In addition, due to a protection effect of Mt layers for the decomposition of TC, decomposition temperature of TC increased about tens of degrees on Mt-TC. This conclusion was in great agreement with previous findings about the decomposition of intercalated organic cations (Xi et al. 2005;Zhu et al. 2008). Finally, the temperature for carbonization of the Mt-TC nanocomposite was settled at 700°C to achieve a greater degree of graphitization in the formed carbonaceous material.

From Fig.2, the d_{001} spacing of raw Mt was 15.5 Å, indicating that the interlayer cation was Ca^{2+} with two layers of water associated with the hydration of calcium. After the contact with TC solution, a significant shift of the 001 reflection to a lower angle could be observed and the basal spacing of Mt-TC reached 21.1 Å, suggesting the TC intercalation in the interlayer space. After pyrolysis, basal spacing of the obtained Mt-TC-C composite significantly decreased to 14.4 Å, which indicated that an intercalated material of 4.8 Å (14.4 - 9.6 Å) thickness formed between the Mt layer taking into account that the elemental silicate sheet is 9.6 Å (Ruiz-Garcia et al. 2013). The liberated carbon material (TC-C-4-700) showed a 002 reflection of a graphitic carbon, which included two components at 2θ of 26.5° ($d=3.35$ Å) and 25.3° ($d=3.52$ Å), respectively. The former was attributed to ordered graphite crystals and the latter was related to an interlayer spacing of lattice-damaged crystals (dot in inset of Fig.2); this was a multi-phase or heterogeneous graphitization. The graphitic structure of TC-C were further demonstrated from Raman spectroscopy, as showed in Fig.S1. According to the above results, the TC intercalated in the interlayer space of Mt had transformed into a carbon monolayer (*i.e.* graphene-like carbon material) during pyrolysis process. In addition to this type of carbon located at the interlayer space, carbon was also formed between the clay particles, agglomerating them in agreement with SEM observations.

The morphology of the obtained samples were characterized by field-emission SEM (FE-SEM) and TEM measurements. As shown in Fig. 3a and 3b, the TC adsorbed on Mt were converted into carbon materials, which exhibited a layered

texture. After the removal of Mt substrates, the FE-SEM image (Fig. 3c) of TC-C showed ultrathin graphene-like nanosheets and a porous structure composed by the aggregation of thin carbon sheet. TC-C was made up of many ultrathin nanosheets (Fig. 3e), which resembled the morphology of graphene and small crystalline domains with lattice spacings of about 0.35nm (Fig. 3f), which further proved the formation of graphene-like nanosheets. Previous studies reported that carbon materials with similar morphology were prepared from polymer precursors (Bakandritsos 2004; Fernandez-Saavedra et al. 2008).

The element doping can be directly unraveled by the elemental mapping images. One can see that a uniform distribution of C, N and O in TC-C was realized according to Fig. S2, which was well agreement with the result of XPS characterizations. The presence of Si and Cl could be ascribed to the incompletely removed elements that inherited from Mt and the introduction of acid washing process, respectively. From the survey spectra in Fig. 4a, one can see three typical peaks of C 1s, N 1s and O 1s. In order to investigate the effect of Mt on the pyrolysis process of adsorbed TC, we analyzed the N 1s high-resolution spectrum of TC-C-pure (pure TC was placed in a quartz boat and then were pyrolyzed under the same condition. The obtained carbon material denoted as TC-C-pure) to make a comparison. As shown in Table 1, the N content of TC-C was higher than that observed with TC-C-pure. From Fig. 4b, the N 1s high-resolution spectrum of TC-C-pure was deconvoluted into two components, corresponding to pyridinic N at 398.2 eV and pyrrolic N at 399.5 eV. However, for TC-C, the N 1s high-resolution spectrum was deconvoluted into four components

(inset, Fig 4b), corresponding to pyridinic N at 398.3 eV, pyrrolic N at 399.5 eV, graphitic N at 401.5 eV and pyridinic oxide (pyridinic N⁺-O⁻) at 402.4 eV, respectively (Jiang et al. 2014). Noted that, in TC-C-pure, pyrrolic N and pyridinic N were the major species without graphitic N and pyridinic oxide; yet with the effect of Mt, after pyrolysis, graphitic N became the major form of nitrogen doping and the content of pyrrolic N decreased significantly with the increasing content of pyridinic N. These results of XPS suggested the successful incorporation of nitrogen into carbon skeletons during pyrolysis process. As reported in previous study, pyridinic N and graphitic N are generally considered to be primarily responsible for the electrochemical activity in ORR (Ding et al. 2013; Geng et al. 2011; Lai et al. 2012; Zhang et al. 2014). Thus, the obtained carbon materials can be regarded as a potentially promising catalyst in the next generation alkaline fuel cells. –

To further investigate the obtained carbon materials, we conducted N₂ adsorption/desorption analysis. The TC-C had a BET surface area of 326 m²·g⁻¹, a pore volume of 0.27 cm³·g⁻¹ and the pore diameters were centered around 4 nm, as demonstrated by the pore size distribution curve (Fig.5). From inset in Fig.5, the nitrogen adsorption-desorption isotherm for TC-C exhibited a type IV curve. TC-C could evidently adsorb N₂ at different relative pressure, which suggested that TC-C simultaneously contains micropores and mesopores. Moreover, the adsorption isotherm and the desorption isotherm were not overlapped and thus formed H₃-type hysteresis loop, indicative of the narrow slit-like pores created by the stacking of microparticles (Liu et al. 2014). Consistent result can be seen in the pore-size

distribution curve (Fig.5) and the pore diameters were centered around 4 nm.

Therefore, the carbon material should be of layered structure, consistent with the Mt template.

3.2 Electrochemical performance and influencing factors analysis

3.2.1 Electrocatalytic properties towards ORR

The ORR activity of TC-C was first assessed using CV with the potential from -1.0V to +0.2V (vs Ag/AgCl) in O₂- and N₂-saturated 0.1M KOH solution at a scan rate of 10 mV·s⁻¹. As depicted in Fig. 6a, compared to the CV curve when the electrolyte was saturated with N₂, the TC-C showed an oxygen reduction peak at -0.2V when the electrolyte was saturated with O₂, which significantly indicated the reduction reaction was obviously appeared on TC-C electrode in O₂ ambience.

According to the results of the RRDE voltammograms of GC electrodes modified with TC-C and commercial 20 wt% Pt/C at a rotation rate of 1600 rpm in O₂-saturated 0.1M KOH(Fig. 6b), the polarization curve of TC-C indicated that the ORR onset potential on TC-C electrode was at -0.18V (vs Ag/AgCl), the limiting diffusion current at -0.8 V was 2.4 mA·cm⁻² and the value of the half-wave potential (E_{1/2}) was -0.33 V (vs Ag/AgCl). When compared to 20 wt% Pt/C, the ORR activity performance of TC-C, including the value of onset potential, the limiting diffusion current and E_{1/2}, was still not as good as that of commercial Pt/C. A further investigation on the ORR process of TC-C was performed by LSV measurements in O₂-saturated 0.1M KOH electrolyte at different rotation speeds. As showed in Fig.6c, current density increased with an increase of rotation speed as a result of the enhanced

oxygen transport at the electrode surface, indicating diffusion controlled process. The corresponding Koutecky-Levich plots (J^{-1} vs. $\omega^{-1/2}$) displayed good linearity, reflecting the first-order reaction kinetics toward the concentration of dissolved oxygen for TC-C sample. The number (n) of transferring electron during ORR for TC-C is analyzed by the Koutecky-Levich method (Zheng et al. 2013), as shown in Supporting Information. The slopes remained approximately constant over the electrode potentials range between -0.4 and -0.8 V, suggesting that the electron transfer numbers (n) during ORR at different electrode potentials were similar. The n was obtained from the slope of the K-L plots to be 3.39 at -0.7V for TC-C, suggesting that the ORR largely proceeded via the four-electron route, which is comparable to Pt/C catalyst. (El-Deab et al. 2005; Gao et al. 2015)

Considering the commercialization of fuel cells, a high catalytic selectivity of the new ORR catalyst for cathode reactions is important to prevent possible fuel-crossover effects, especially in the use of small-molecule organic fuels, such as methanol, which could crossover through the polymer electrolyte membrane from anode to cathode, seriously compromising the whole cell performance (Qu et al. 2010). The tolerance against methanol crossover of TC-C and Pt/C catalysts towards the ORR was evaluated by chronoamperometric measurements at +0.4 V and a rotation speed of 900 rpm in a 0.1 M KOH solution saturated with O_2 . From Fig. 6e, one can see that no noticeable response was observed in the ORR current at TC-C electrode when the addition of 3 M methanol into the electrolyte, suggesting a good tolerance to the methanol crossover effect. However, the ORR current at the Pt/C electrode

suffered a sharp decrease under similar conditions. Herein, the TC-C catalyst exhibited remarkably enhanced tolerance against methanol crossover, as compared to Pt/C. In terms of the results of LSV measurements, the ORR performance of TC-C was not as efficient as that of the commercial 20 wt% Pt/C catalyst. However, TC-C proceeded largely with a four-electron transfer pathway in ORR, which calculated from the data based on LSV measurements. Besides, as a metal-free catalyst, the TC-C exhibited better methanol tolerance during oxygen reduction compared with the commercial Pt/C catalysts.

3.2.2 Influence of the adsorbed TC amount on ORR activity of TC-C

The adsorption of TC on clay mineral such as Mt has been studied since 1950s and factors influencing the adsorption TC on Mt, including pH, ionic strength, coexistence cation and humic acid, also have been extensively investigated (Zhao et al. 2012). The amount of adsorbed TC on Mt were different under various conditions. Therefore, from the point of reuse of the spent Mt, the effect of the amount adsorbed TC on the properties of TC-C is considered as an important factor. As shown in Fig.S3a (inset), TC adsorbed on Mt at different initial concentration (2, 4 and 8 g·L⁻¹) was 204, 330 and 611 mg·g⁻¹, respectively. Fig.S3a showed the LSVs of TC-C-2-700, TC-C-4-700 and TC-C-8-700 at a rotation rate of 1600 rpm in O₂-saturated 0.1M KOH. The onset potential is -0.13 V for TC-C-4-700, -0.16 V for TC-C-2-700 and -0.16 V TC-C-8-700, respectively, and the limiting diffusion current density at -0.5 V increased in the order of 1.51 mA·cm⁻² (TC-C-4-700) < 1.61 mA·cm⁻² (TC-C-2-700) < 1.98 mA·cm⁻² (TC-C-4-700). These results suggested that the sample of

TC-C-4-700 exhibited the best performance of ORR activity among the series.

Considering the factors such as a BET surface area and the content of N, which play a role in the ORR activity, the differences among the series were analyzed (Table S1).

The BET surface area of them were around at $370 \text{ m}^2 \cdot \text{g}^{-1}$ and the content of N for TC-C-4-700 (2.00%) is the highest. In addition, the results of high-resolution N 1s spectra for the series suggested that TC-C-4-700 showed the highest content of graphitic N (50.32%), which has been proposed to be mainly responsible for the ORR activity (Fig.S3b). Hence, the above results were consistent with the result of LSVs. However, considering the practical utilization of by-product obtained from the spent Mt, the little difference among these samples could be neglected. Therefore, the influence of the amount adsorbed TC on the ORR activity of TC-C is slight and can be neglected.

3.2.3 Influence of the pyrolysis temperature on ORR activity of TC-C

Pyrolysis temperature is considered to be also another important factor that influencing the ORR activity of the catalyst. As showed in Fig.S4a, the onset potential was -0.11 V for TC-C-4-700, which was more positive than that of TC-C-4-600 and was the same as that of both TC-C-4-800 and TC-C-4-900. The limiting diffusion current density at -0.5 V increased in the order of $1.33 \text{ mA} \cdot \text{cm}^{-2}$ (TC-C-4-600) < $1.84 \text{ mA} \cdot \text{cm}^{-2}$ (TC-C-4-800) $\approx$ $1.85 \text{ mA} \cdot \text{cm}^{-2}$ (TC-C-4-900) < $1.98 \text{ mA} \cdot \text{cm}^{-2}$ (TC-C-4-700). Therefore, the best performance of ORR activity was observed with the samples prepared at a heating temperature of 700°C. From Table S2, the BET surface area of the series samples decreased with the increasing pyrolysis temperature and the content

of N increased in the order of 1.38% (TC-C-4-900) < 1.92% (TC-C-4-600) < 2.00% (TC-C-4-700) < 2.37% (TC-C-4-800). Take the high-resolution N 1s spectra of the samples into consideration, one could see that the content of graphitic N (50.32%) for TC-C-4-700 was the highest among the series (Fig.S4b). Therefore, a higher content of N and BET surface area didn't lead to better performance and the content of graphitic N is a crucial factor influencing the ORR activity for the series of TC-C samples. In addition, the pyrolysis temperature of 700°C can be regarded as the optimal temperature for the pyrolysis process in the recycling of spent Mt.

3. 3 Reasons accounting for the suboptimal ORR activity of TC-C

In terms of the physicochemical characterization of TC-C, the TC-C sample can be named as N-doped graphene-like carbon materials. The reasons, which can account for the superior ORR electrocatalytic activity of N-doped carbon materials, can be summarized as followed: (1) structural and morphological properties; (2) macroscopic, mesoporous and microscopic structures ; (3) nitrogen doping level and the content of different nitrogen types (graphitic N, pyridinic N and pyrrolic N) (Zhi et al. 2013). The sample of TC-C, which was consisted of ultrathin graphene-like nanosheets, had a BET surface area of $326 \text{ m}^2 \cdot \text{g}^{-1}$ and a pore volume of $0.27 \text{ cm}^3 \cdot \text{g}^{-1}$. In addition, the high resolution XPS pattern of N 1s spectrum of TC-C showed the simultaneous presence of graphitic N, pyridinic N and pyrrolic N. Graphitic N atoms have been reported to accelerate ORR due to their high activity sites both experimentally and theoretically (Kim et al. 2011;Lai et al. 2012). Lai's report suggested the pyridinic N atoms might convert the ORR reaction mechanism from a 2e dominated process to a

4e dominated process and improve the ORR onset potential (E_{onset})(Lai et al. 2012). Therefore, TC-C exhibited good electrocatalytic activity for ORR and showed the potential to be the metal-free ORR catalysts. As shown in Table S3, the ORR activity of TC-C was better than that of NB-graphene (Dou et al. 2014), close to that of C-800(Zhu et al. 2015) and CH-mel (Rybarczyk et al. 2015), and not efficient as that of SF-NMGF (Ye et al. 2015), respectively. The suboptimal catalytic performance of TC-C could be a result of (1) the low nitrogen content, and (2) the inevitable presence of impurity despite of repeated acid washing process. However, considering the concept of this work, we used the TC adsorbed on Mt as precursor and fully utilized the template effect of Mt to offer protection for carbonizing TC. Moreover, we disposed the spent Mt to achieve the aim of reducing secondary environmental problems; on the other hand, we obtained a by-product surprisingly, which could be used as efficient metal-free electrocatalyst in fuel cells.

4 Conclusion

A facile and low cost pyrolysis strategy was used to dispose the spent Mt after the adsorption of TC and obtained a kind of by-product, N-doped graphene-like carbon-based electrocatalysts, for ORR in fuel cells. The FE-SEM and TEM images showed that TC-C was made up of many ultrathin nanosheets, which resembled the morphology of graphene and Raman spectra demonstrated the presence of both D-band and G-band on TC-C. Nitrogen doping was evaluated through XPS measurements and four nitrogen-bonding configurations were identified and quantified, including pyridinic N, pyrrolic N, graphitic N and pyridinic $\text{N}^+\text{-O}^-$. The

results of nitrogen adsorption/desorption measurements suggested the presence of the narrow slit-like pores created by the stacking of microparticles in TC-C with a high BET specific surface area about $326 \text{ m}^2 \cdot \text{g}^{-1}$. Furthermore, our study indicated that effect of the amount adsorbed TC on ORR activity of TC-C was negligible and the pyrolysis temperature of 700°C could be regarded as the optimal temperature for the pyrolysis process of Mt-TC nanocomposite in recycling of the spent Mt. Our work built a link between the appropriate disposal of spent adsorbent and the requirement to develop more sustainable sources of energy.

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Figures

Fig.1 TG and DTG curves of (a) TC and (b) TC-Mt

Fig.2 XRD patterns of (a) Mt, (b) Mt-TC-4, and (c) Mt-TC-C-4-700; inset shows XRD pattern of TC-C-4-700

Fig.3 (a and c) FE-SEM images of Mt-TC-C and TC-C, respectively (inset b, FE-SEM image of Mt-TC composite). (e) TEM image of TC-C. (f) HR-TEM image of TC-C.

Fig.4 (a) XPS survey of TC-C; (b) High-resolution N 1s XPS spectra of TC-C-pure TC; inset shows high-resolution N 1s XPS spectra of TC-C

Fig.5 (inset) N₂ adsorption-desorption isotherms and corresponding pore size distribution curve of TC-C

Fig.6 (a) Cyclic voltammograms of a glassy carbon electrode modified with TC-C in O₂-saturated and N₂-saturated 0.1 M KOH at a scan rate of 10 mV·s⁻¹, respectively; (b) RRDE voltammograms of a glassy carbon electrode modified with TC-C and Pt/C at the rotation rate of 1600 rpm. Scan rate: 10 mV·s⁻¹; (c) Steady state polarization curves of O₂ reduction for TC-C in O₂-saturated 0.1M KOH at different rotation rates. Ring potential was set at +0.5 V. Potential scan rate was 10 mV·s⁻¹. (d) Koutecky-Levich plots of TC-C at different electrode potentials. (e)

Chronoamperometric responses of TC-C and Pt/C electrodes with the addition of 3M methanol

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