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### PAPER

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## Silicon carbide supported iron nanoparticles encapsulated in nitrogen-doped carbon for oxygen reduction reaction

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Silicon carbide (SiC) was extracted using CCl<sub>4</sub> and NH<sub>3</sub> at 800 °C to form SiC core with derived nitrogen-doped carbon shell (SiC@N-C), which is explored as supporting material for iron nanoparticles encapsulated in nitrogen-doped carbon (Fe@N-C) due to its excellent corrosion resistance. The carbon shell around SiC is essential to successfully grow Fe@N-C around SiC@N-C during pyrolysis of cyanamide and iron acetate. In sharp contrast, Fe<sub>3</sub>Si supported on SiC was obtained using pristine SiC as the supporting material. Fe@N-C/SiC@N-C showed much higher activity for oxygen reduction reaction than SiC@N-C and Fe<sub>3</sub>Si/SiC, even exceeding commercial Pt/C catalyst in alkaline medium. Furthermore, Fe@N-C/SiC@N-C also demonstrated higher durability and methanol resistance than Pt/C catalyst.

#### Introduction

Exploring highly active and durable catalysts for oxygen reduction reaction (ORR) is of fundamental importance for the research and development of fuel cells and metal-air batteries.<sup>1-5</sup> Carbon supported Pt-based catalysts have demonstrated high activities toward ORR in both acidic and alkaline mediums.<sup>6, 7</sup> However, they suffer from severe corrosion of carbon support under high cathode potential and oxidative atmosphere, resulting in aggregation of Pt nanoparticles (NPs) and insufficient durability.<sup>8</sup> Furthermore, the high cost and terrestrial scarcity of Pt resources hinder its extensive use in fuel cells and metal-air batteries.<sup>5, 9</sup> Therefore, development of non-precious metal catalysts with high activity and durability is urgently demanded to address the major issues currently plaguing ORR.<sup>10-15</sup>

Silicon carbide (SiC), possessing excellent oxidation and acid corrosion resistance, has been used as the supporting material for Pt NPs for catalyzing ORR.<sup>16-18</sup> The durability of nano-sized SiC supported Pt NPs is significantly improved compared with Pt/C catalyst.<sup>19</sup> However, the electrical conductivity of SiC is insufficient, and incorporation of carbon black by mechanical mixing is usually necessary to improve the electrical conductivity of Pt/SiC catalysts.<sup>2</sup> As a more effective route, Si atoms can be partially extracted away from SiC by high-temperature vacuum annealing, acid etching or chlorinating, resulting in epitaxial growth of carbon shell around the residual SiC to form a core-shell structured SiC@C composite material.<sup>21-24</sup> The SiC@C has an improved electrical conductivity while still retaining high thermal and chemical stabilities compared with SiC.25, 26 The Pt/SiC@C catalysts demonstrate enhanced durability for ORR, which is attributed to the anchoring effect of carbon shell to Pt NPs and the high corrosion resistance of SiC core.21

SiC has been also explored as the support of nitrogen-doped carbon (N-C) material for catalyzing ORR in alkaline medium, and

the core-shell structured SiC@N-C was prepared by acid etching and successive nitrogen doping using melamine as nitrogen precursor at 1300 °C.<sup>27</sup> The metal-free SiC@N-C shows promising activity and durability for ORR. Recently, we have developed a novel class of transition metal NPs encapsulated in N-C for effectively catalyzing ORR<sup>10, 28, 29</sup>. The transition metal NPs greatly increases the graphitization degree of carbon materials and an encapsulation structure is simultaneously formed during carbonization.<sup>29</sup> The surface carbon shell prevents acid-leaching, oxidation and aggregation of transition metal NPs in the electrocatalytic process, possessing excellent durability in a wide pH range.<sup>28</sup> A synergetic role of doped nitrogen in carbon lattice and the encapsulated transition metal NPs stimulates an enhanced intrinsic electrocatalytic activity on the carbon-based materials.<sup>29</sup> Considering the unique merits of SiC, we explored SiC as the supporting material for iron NPs encapsulated in nitrogen-doped carbon (Fe@N-C). It was observed that the formation of N-C shell around the SiC was essential to grow Fe@N-C with carbon nanotube morphology around SiC@N-C, whereas Fe<sub>3</sub>Si was obtained when using pristine SiC as the supporting material. Fe@N-C/SiC@N-C composite material showed high ORR activity in alkaline medium, along with high durability and methanol tolerance compared with the state-ofart Pt/C catalyst.

#### **Experimental section**

SiC@N-C material was synthesized according to the procedures reported previously.<sup>30, 31</sup> 0.7 g of SiC granules ( $\alpha$ -phase, Alfa Aesar Chemical Ltd.) were placed in a quartz tube of a perpendicular furnace. The furnace was heated to 800 °C at a rate of 5 °C/min in Ar atmosphere with a flow rate of 50 mL/min. Then Ar was switched into a bottle filled with CCl<sub>4</sub> and mixed with NH<sub>3</sub> (the flow rate ratio of NH<sub>3</sub> to Ar was 1:1) before passing through the SiC granules. The

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temperature was kept at 800 °C for 1 h. Then the atmosphere was recovered to pure Ar and cooled to room temperature. The obtained sample is denoted as SiC@N-C.

1.75 g of cyanamide and 0.5 g of iron acetate were dissolved in 60 mL of ethanol and stirred for 3 h at 60 °C. Then 0.1 g of SiC@N-C was added to the solution and stirred at 60 °C overnight. The solvent was evaporated at 45 °C and the obtained mixture was placed in a quartz tube of a horizontal furnace and pyrolyzed at 950 °C for 1 h in Ar atmosphere with a flow rate of 100 mL/min. The product was leached in 0.5 M HClO<sub>4</sub> solution at 80 °C for 8 h to remove unstable Fe species, and washed with de-ionized water thoroughly. Finally, the sample was dried at 60 °C in an oven, and is denoted as Fe@N-C/SiC@N-C. For comparison, as-received pristine SiC was used instead of SiC@N-C to pyrolyze under identical conditions, and the product is denoted as Fe<sub>3</sub>Si/SiC.

X-ray diffraction (XRD) was performed on a Rigaku D/Max-2500 diffractometer with a Cu K $\alpha$  radiation source ( $\lambda$ =1.5418 Å) at 40 kV and 200 mA at a scan rate of 5°/min. The morphologies of the samples were investigated by an FEI Tecnai G<sup>2</sup> microscope at 120 kV and a JEOL JEM-2100 microscope at 200 kV, respectively. Xray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific spectrometer with an Escalab 250 Xi X-ray as excitation source. Thermogravimetry (TG) measurements were performed on a TGA-DSC analyzer (NETZSCH STA 449 F3 Jupiter®). Dry air provided by a pressured tank with a flow rate of 50 mL/min was used as the carrier gas. The experiments were carried out from room temperature to 900 °C with a heating rate of 10 °C/min. Nitrogen adsorption/desorption was carried out using a Quantachrome QUADRASORB SI system at 77 K, and specific surface areas of the samples were calculated by the Brunauer-Emmet-Teller (BET) equation.

Electrochemical measurements were carried out in a 150 mL three-electrode cell (AKCELL3, Pine Research Instrumentation) at 25 °C. A commercial glassy carbon (GC) electrode (AFE2M050GC, 5 mm in diameter, 0.196 cm<sup>2</sup>, Pine Research Instrumentation) covered by the sample with Nafion ionomer as a binder and a graphite rod electrode were used as the working electrode and counter electrode, respectively. An Hg/HgO electrode (Shanghai Yueci Electronic Technology Co. Ltd.), calibrated vs. reversible hydrogen electrode (RHE) in 0.1 M KOH solution, was used as the reference electrode. All potential values in this paper are referred to compare with the RHE. The rotation rate and the potential of the working electrode were controlled by a MSR Electrode Rotator (Pine Research Instrumentation) and an Autolab potentiostat /galvanostat (PGSTAT 302N). 10 mg of the catalyst was dispersed in a mixture of 0.5 mL de-ionized water (18.2 MQ·cm, Millipore), 2 mL isopropanol and 50 µL of Nafion solution (5 wt %) with ultrasonic stirring to form a homogenous ink. The catalyst layer was prepared by dropping 50 µL of the ink onto a GC disk electrode by a pipette and drying at room temperature. The ORR activities of the catalysts were evaluated by rotating disc electrode (RDE) measurement in O2-saturated 0.1 M KOH solution with a scan rate of 10 mV/s. Linear sweep voltammetry (LSV) data were recorded at a rotation rate of 2500 rpm.

For accelerated aging test (AAT), after the initial linear sweep voltammentry (LSV) curve was recorded in  $O_2$ -saturated 0.1 M KOH solution, the working electrode was transferred to Ar-saturated 0.1 M KOH solution. CV measurements were conducted at a scan rate of 100 mV/s in a potential range of 0.6~1.0 V. After 5000 cycles, the working electrode was transferred back to  $O_2$ -saturated 0.1 M KOH solution for LSV measurements. For methanol poisoning experiment, chronoamperometric measurement was performed at 0.745 V (vs. RHE) in 0.1 M KOH solution at a rotation rate of 2500 rpm. Ar was purged into the electrolyte solution for 30

min prior to the chronoamperometric measurement, and was kept purging during the first 600 s in the measurement. After 600 s,  $O_2$ was introduced to purge into the electrolyte solution. And after 3000 s, 2% (v/v) methanol was injected into the electrolyte solution to investigate the effect of methanol poisoning on the ORR current. The whole chronoamperometric measurement lasts 5000 s. In the above electrochemical measurements, Pt/C (Tanaka Kikinzoku Kogyo, 37 wt. % Pt) was used for comparison and the loading of Pt/C was 50 µg/cm<sup>2</sup> for electrochemical measurements.

#### **Results and Discussion**

Fig. 1 shows XRD patterns of the samples. The SiC granules have strong diffraction peaks correspond to its different facets (JCPDS, No. 29-1128). The broad peaks at 26.1° and 43° in SiC@N-C are assigned to diffractions from the (002) and (100) planes of the hexagonal structure of graphite while the diffraction peaks of SiC are still retained.<sup>32</sup> In Fe@N-C/SiC@N-C, the peak at 43.6° in Fe@N-C/SiC@N-C are probably assigned to diffractions from the (111) plane of diamond-like carbon. The diffraction peaks at 44.7°, 65.0° and 82.3° in Fe@N-C/SiC@N-C indicate the presence of  $\alpha$ -Fe. In Fe<sub>3</sub>Si/SiC, there are diffraction peaks attributed to Fe<sub>3</sub>Si except for the diffraction peaks of SiC with negligible carbon diffraction peaks. The difference between pristine SiC and SiC@N-C is nitrogendoped carbon material, however, results in significantly different composition of iron species in both samples.



Figure 1. XRD patterns of different samples.

TEM and HRTEM images of different samples are shown in Fig. 2. The as-received pristine SiC shows a smooth surface (Fig. S1). After extraction with  $CCl_4$  and  $NH_3$  for 1 h, N-C shell grows around the residual SiC core with a thickness of about 70 nm. HRTEM images of the carbon shell indicate a moderate graphitization degree. After high-temperature pyrolysis of cyanamide and iron acetate with SiC@N-C, the thickness of carbon shell was decreased, and iron NPs encapsulated in carbon nanotube grow on the surface of carbon shell, indicating that the amorphous carbon was etched during the high-temperature pyrolysis. In sharp contrast, there is only amorphous carbon formed around the SiC after pyrolysis of cyanamide and iron acetate, and Fe<sub>3</sub>Si nanoparticles are deposited on the SiC.

TG curves in air atmosphere are shown in Fig. 3. During the heating process, two types of oxidation reactions occur. One is the oxidation of nitrogen-doped carbon to  $CO_2$  and  $NO_x$ , leading to weight loss. The other is the oxidation of Fe to  $Fe_2O_3$  with an increase of weight. The residual materials after TG experiments in





Figure 2. TEM and HRTEM images of (a) (b) SiC@N-C, (c) (d)  $Fe_3Si/SiC$ , (e) (f) Fe@N-C/SiC@N-C.

air atmosphere are Fe<sub>2</sub>O<sub>3</sub> and SiC. After TG experiments, there is a slight increase of 0.8 % in weight on SiC, indicating that partial surface SiC was probably converted into SiO<sub>2</sub>. The mass loss of SiC@N-C mainly occurs in a temperature range from 430 °C to 660 °C, and the content of carbon and nitrogen is 30.8 % obtained from TG results. There is only 8.9 % weight loss on Fe<sub>3</sub>Si/SiC, which is probably attributed to the carbon oxidation, whereas, there is 54.0 % weight loss on Fe@N-C/SiC@N-C, suggesting that SiC@N-C is beneficial for the growth of carbon materials, in agreement with the TEM results.



Figure 3. TG curves of different samples in air atmosphere.

The specific surface area of the samples was measured. SiC and SiC@N-C have low surface areas of 11.0 m<sup>2</sup>/g and 14.1 m<sup>2</sup>/g. The N<sub>2</sub> adsorption-desorption curves of Fe<sub>3</sub>Si/SiC and Fe@N-C/SiC@N-C belong to the isotherms of type IV (based on IUPAC classification) with a hysteresis loop, indicating the existence of mesopores. Because the carbon and nitrogen fragments produced during pyrolysis were deposited on SiC and SiC@N-C to form carbon materials, therefore Fe<sub>3</sub>Si/SiC and Fe@N-C/SiC@N-C have high surface areas of 52.1 m<sup>2</sup>/g and 75.4 m<sup>2</sup>/g.



Figure 4. Nitrogen adsorption-desorption isotherm of different samples.

The ratio of doped nitrogen to carbon in the samples is measured by XPS. There is negligible N1s signal in Fe<sub>3</sub>Si/SiC (Fig. S2) despite that Fe<sub>3</sub>Si/SiC is obtained from nitrogen-rich cyanamide. There is no graphitized carbon shell present in the pristine SiC support as a matrix for hosting nitrogen and carbon fragments. Under the high reductive atmosphere, iron species react with SiC to form Fe<sub>3</sub>Si, and then amorphous carbon segregates on the surface. The content of nitrogen in SiC@N-C and Fe@N-C/SiC@N-C is 5.9 wt.% and 3.0 %, respectively. A part of doped nitrogen in SiC@N-C is released together with carbon by high-temperature pyrolysis at 950 °C, thus the content of doped nitrogen in Fe@N-C/SiC@N-C decreased.

The ORR activities of the samples are assessed in O<sub>2</sub>-saturated 0.1 M KOH solution, as shown Fig. 5. SiC shows the poorest activity for ORR, and SiC@N-C and Fe<sub>3</sub>Si/SiC also show inferior activities. In contrast, Fe@N-C/SiC@N-C demonstrates obvious positive shift on the onset potential for ORR at 0.88 V and high cathodic current density. Fe@N-C/SiC@N-C, having a low content of doped nitrogen, shows a much higher ORR activity than SiC@N-C, which suggests that Fe@N-C/SiC@N-C.<sup>14</sup> Interestingly, Fe@N-C/SiC@N-C shows slightly higher ORR activity than Pt/C in 0.1 M KOH solution. We have compared the ORR activities of the reported non-previous metal catalysts, as listed in Table S1. Fe@N-C/SiC@N-C shows high ORR activity amongst the reported non-precious metal catalysts.<sup>33-35</sup>



Figure 5. LSV curves of different samples in O<sub>2</sub>-saturated 0.1 M KOH solution at 25 °C. Rotation rate: 2500 rpm.

Fig. 6 shows linear sweep voltammetrograms of Fe@N-C/SiC@N-C at different rotation rates. The Koutecky-Levich plots present the relationship of  $j^{-1}$  versus  $\omega^{-0.5}$ , where j represents the measured current density, and  $\omega$  is the rotation rate of the electrode. The limiting current density increases with the rotation rate, indicative of an improved mass transport.<sup>36</sup> The curves of Fe@N-C/SiC@N-C at different potentials are shown in Fig. 6b to investigate the ORR kinetics. All six plots display linear and relatively parallel behaviour, implying one-order kinetics with respect to oxygen concentration. The measured n is 3.6 for Fe@N-C/SiC@N-C, indicative of a mixture of a four-electron route and a "two + two" route in alkaline medium.<sup>37</sup>



Figure 6. (a) LSV of Fe@N-C/SiC@N-C in O<sub>2</sub>-saturated 0.1 M KOH solution at a scan rate of 10 mV/s with different rotation rates and (b) K-L Plot of Fe@N-C/SiC@N-C at different potentials.

The durability of Fe@N-C/SiC@N-C was evaluated by cycling between 0.6 V and 1.0 V, and Pt/C was also measured as a reference material, as shown in Fig. 7. After 5000 continuous cycles, the ORR activity of Fe@N-C/SiC@N-C only slightly decreases, while that of Pt/C declines obviously. Fig. 7b shows the ratio of current density before and after 5000 cycles at different potentials. At 0.9 V, the ratio of Fe@N-C/SiC@N-C and Pt/C is 0.97 and 0.56, respectively. Fe@N-C/SiC@N-C shows a much higher cycling stability, which can be ascribed to the unique encapsulation structure of iron nanoparticles within highly graphitized carbon nanotube.

The methanol resistance of Fe@N-C/SiC@N-C during ORR was evaluated and the results were also compared with the Pt/C catalyst. As shown in Fig. 8, after switching the purge gas from Ar to  $O_2$  at 600 s, the current density on Fe@N-C/SiC@N-C and Pt/C increases immediately, indicating that ORR occurred on both catalysts. After the current on both catalysts is stabilized, 2 % (v/v) methanol was injected into the electrolyte solution at 3000 s, and the current on the Pt/C catalyst drops quickly. The observed decrease of current on the Pt/C catalyst is a result of methanol oxidization at the cathode. In contrast, the current on Fe@N-C/SiC@N-C does not

vary much with the injection of methanol. The improved methanolresistance ability is probably due to the core-shell structure of Fe@N-C/SiC@N-C. The carbon wrapping layer protects the core nanoparticles from direct contacting with methanol contaminants.



Figure 7. (a) LSVs of Fe@N-C/SiC@N-C and Pt/C before and after 5000 potential cycles between 0.6 to 1.0 V (vs. RHE) and (b) the ratio of current after 5000 cycles to initial current for Fe@N-C/SiC@N-C and Pt/C at different potentials.



Figure 8. The relative current–time response of Fe@N-C/SiC@N-C and Pt/C catalyst in 0.1 KOH solution at 0.745 V (vs. RHE). O<sub>2</sub> was switched to purge into the electrolyte solution at 600 s. 2% (v/v) methanol was injected into the electrolyte solution at 3000 s.

#### Conclusion

SiC-supported Fe@N-C composite material was prepared by pyrolysis of the mixture of SiC@N-C, cyanamide and iron acetate. The carbon shell in SiC@N-C is essential to grow Fe@N-C around SiC@N-C, whereas Fe<sub>3</sub>Si with negligible carbon is formed when

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using pristine SiC as the supporting material. Iron nanoparticles encapsulated in nitrogen-doped carbon nanotubes grew on the carbon shell of SiC@N-C. Fe@N-C/SiC@N-C composite material showed a positive onset potential and enhanced limiting current density over SiC@N-C and Fe<sub>3</sub>Si/SiC, highlighting important contributions of Fe@N-C to ORR activity. Compared with commercial Pt/C catalyst, Fe@N-C/SiC@N-C demonstrated higher ORR activity, much better durability and methanol resistance.

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**Graphical Abstract** 

Iron nanoparticles encapsulated in nitrogen-doped carbon (Fe@N-C) supported on SiC core with derived nitrogen-doped carbon shell (SiC@N-C) shows much higher activity for oxygen reduction reaction than SiC, SiC@N-C and SiC-supported Fe<sub>3</sub>Si, even exceeding commercial Pt/C catalyst in alkaline medium.