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ARTICLE TYPE

A hybrid of titanium nitride and nitrogen-doped amorphous carbon supported on SiC as a noble metal-free electrocatalyst for oxygen reduction reaction

Yingdan Jia,[a] Yanhui Wang,[a] Liang Dong,[a] Junjie Huang,[a] Yan Zhang,[a] Jing Su[a] and Jianbing Zang*[a]

A novel noble metal-free catalyst, with nitrogen-doped amorphous carbon and titanium nitride particles supported on SiC (NC-TiN/SiC), was synthesized. The NC-TiN/SiC
10 **exhibited excellent oxygen reduction reaction activities as well as superior stability and methanol tolerance. The catalytic activities were attributed to the synergistic effect of TiN and NC.**

The polymer electrolyte membrane fuel cells (PEMFCs) are
15 considered to be one of the most promising alternatives to conventional power sources for its high efficiency and low environmental impact. Oxygen reduction reaction (ORR) as a cathodic process is usually considered as a dominant factor for improving the overall performances of PEMFCs because of its
20 sluggish kinetics[1-3]. Currently, carbon supported platinum (Pt/C) electrocatalysts are commonly used to accelerate the ORR due to their high activities. However, the high costs and relative scarcity of the Pt metal become major obstacles for commercial applications of fuel cells.[4] Thus, it is imperative to explore low-
25 cost, high efficient and stable noble metal-free catalysts for ORR to perform the commercialization of PEMFCs.

In recent years, various noble metal-free catalysts have been explored, such as transition-metal organic macrocycles, nitrides, oxides, carbides and heteroatoms (as nitrogen) doped
30 carbonaceous materials.[5-8] Among them, nitrogen (N)-doped carbon materials, such as N-doped carbon nanotubes and N-doped graphene, were extensively demonstrated as effective metal-free electrocatalysts for ORR. It can greatly improve the ORR activity by incorporating of N atoms into carbon matrix.[9] In
35 addition, the low cost transition metal nitrides, especially titanium nitride (TiN), were also proved to be promising materials in PEMFCs for their similar electronic structure to noble metals and high electrical conductivity and corrosion resistance.[10] However, nano-sized TiN is liable to agglomerate, so it is usually modified
40 with carbon-based materials. There have been a few of reports about carbon-coated TiN, or TiN supported on carbon nanotubes or graphene as efficient electrocatalyst for ORR.[11,12] The defect is that these sp^2-bonded carbon materials are susceptibly oxidized under electrochemical conditions, leading to a microstructural
45 degradation of catalysts and a deteriorative long-term performance. Nano-SiC possessing high mechanical strength and stability in oxidative environments, could be used as an alternative support to improve catalyst stability.[13]

In this report, we prepared a hybrid of nano TiN and nitrogen-
50 doped amorphous carbon (NC) using nano-SiC as a stable support (NC-TiN/SiC). The formation of NC was expected to promote the catalytic activity of ORR in harmony with TiN, integrate the SiC and TiN particles to reduce the TiN agglomeration and improve the electrical conductivity for fast
55 transport of electrons. In addition, NC-TiN/SiC was expected to possess excellent catalytic activities for ORR and high stability.
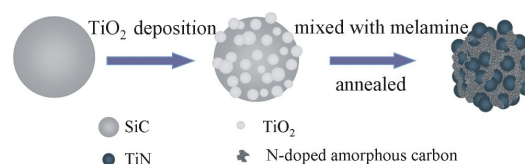
Scheme 1. Illustration of the preparation procedure of NC-TiN/SiC

Scheme 1 shows the formation of the NC-TiN/SiC. Firstly,
60 TiO₂ nanoparticles were deposited on the SiC surfaces using a non-boiling isothermal hydrolyzing process[14] which is developed for preparation of nano crystalline oxides without post-heating treatment for crystallization. And then the SiC-supported TiO₂ (TiO₂/SiC) was heated with melamine under an N₂ atmosphere.
65 During the heat treatment, an amorphous carbon layer was formed on SiC suface and doped with nitrogen atoms simultaneously with nitridation of TiO₂. As a result, a hybrid of TiN and NC supported on SiC (NC-TiN/SiC) was obtained.

Fig. 1 shows the transmission electron microscope (TEM),
70 high-resolution TEM (HRTEM) images and X-ray diffraction (XRD) patterns of TiO₂/SiC and NC-TiN/SiC. In Fig. 1a, small TiO₂ nanoparticles dispersed on the sphere-like SiC particles. The lattice spacings of 0.352 and 0.242 nm in Fig. 1b were assigned to the (101) planes of TiO₂ (anatase) and the (111) planes of SiC,
75 respectively. From Figs. 1c and d, it can be seen that TiN nanoparticles are uniformly distributed on the surface of the SiC particles after nitridation process. Fig. 1e shows a crystal structure with 0.212 nm lattice fringes, which was corresponded to the (111) planes of TiN, confirming the TiO₂ was successfully
80 transformed to TiN by heating the mixture of TiO₂/SiC and melamine. The particle size of TiN is 10~20 nm. These results were in accordance with X-ray diffraction results (Fig. S1and Table S1 in ESI), in which the average grain sizes of TiO₂ and TiN were calculated to be 5.3 and 13.2 nm, respectively.
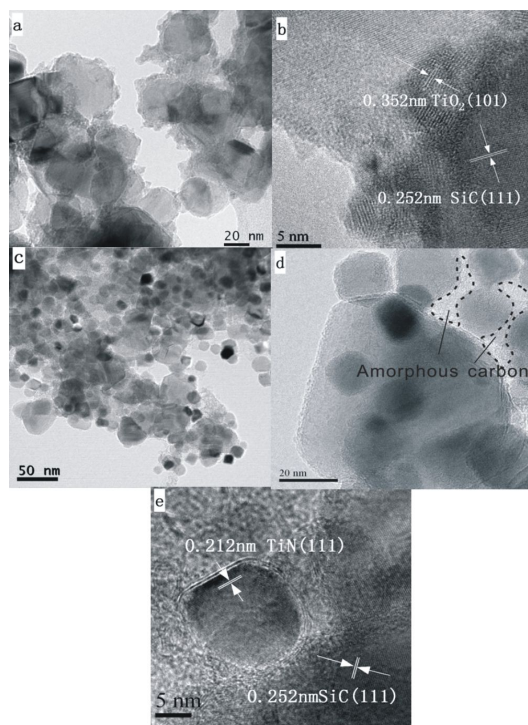
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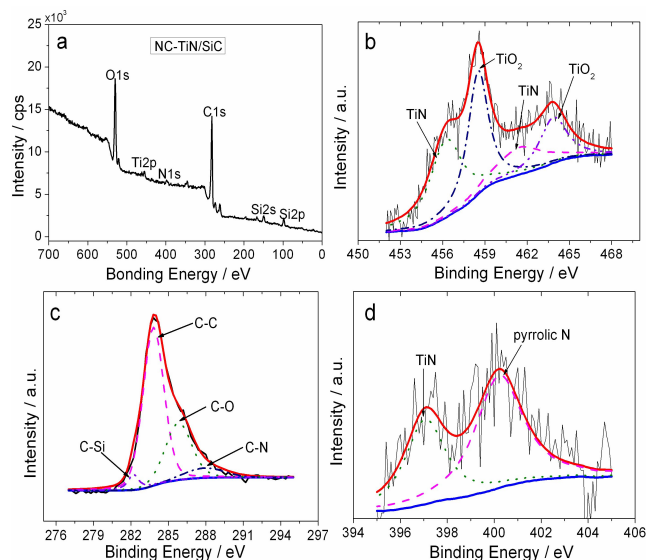Fig. 1 TEM and HRTEM images of (a, b) TiO₂/SiC, (c, d, e) NC-TiN/SiC

5 Fig. 2 XPS survey spectra of (a) NC-TiN/SiC; (b) High resolution Ti 2p, (c) C 1s and (d) N 1s peaks of NC-TiN/SiC

Noteworthily, amorphous carbons were found between or on the surface of TiN particles as well as on the surface of SiC particles, as indicated by the black dashed lines in Fig. 1d.

10 Further information came from X-ray photoelectron spectroscopy (XPS) survey spectra of the NC-TiN/SiC in Fig. 2. In Fig. 2a, the characteristic peaks of Ti 2p, C 1s, O 1s, N 1s, Si 2p and Si 2s appeared at the corresponding binding energies 456.8, 284.4, 532.4, 400.4, 151.6 and 99.6 eV, indicating the

15 presence of Ti, C, O, N and Si elements. The high-resolution spectra of C 1s, N 1s and Ti 2p were well-fitted into several different related peaks, respectively. The Ti 2p level is normally spin–orbit-split into the Ti $2p_{1/2}$ and Ti $2p_{3/2}$ sublevel.[15] In Fig. 2b, the peaks at 458.6 eV in the Ti $2p_{3/2}$ region and 464.2 eV in the
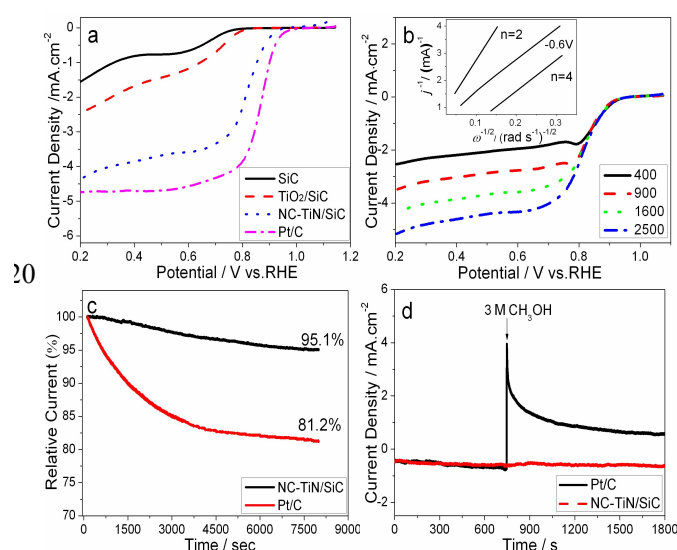

Fig. 3 LSV curves of (a)SiC, TiO₂/SiC, NC-TiN/SiC and Pt/C with a rotation rate of 1600 rpm and (b) NC-TiN/SiC at different rotation rates in O₂-saturated 0.1 M KOH, ν=10mVs⁻¹. (c) I–T curves for NC-TiN/SiC and

25 Pt/C in O₂-saturated 0.1 M KOH at rotation rate of 1600 rpm (d) CA responses of NC-TiN/SiC and Pt/C in O₂-saturated 0.1 M KOH solution with the addition of 3 M methanol at around 750 s.

Ti $2p_{1/2}$ region were generally characteristic of Ti-O and the other two peaks were corresponding to the N-Ti-N in TiN. This

30 confirmed the formation of TiN after the nitridation of TiO₂. The C 1s peak positions in Fig. 2c can be assigned as C-Si at 282 eV, C-C (sp²) at 284.3 eV, C-O at 286 eV and C-N at 287.9 eV. The latter three peaks indicated the presence of sp²-bonded carbon. Furthermore, from Fig. 2d, we can see the N 1s peak was fitted to

35 two components based on 397.4 eV and 400.3 eV binding energies, corresponding to the essential TiN and pyrrolic N. And the pyrrolic N concentration in NC was calculated to be 3 at%. This result, along with the presence of C-N in C 1s peak (Fig. 3c), implied that the amorphous carbons were doped with N atoms.

40 Energy dispersion spectrum analysis (Fig. S2 and Table S2 in ESI) was performed to estimate the chemical composition of the NC-TiN/SiC, which confirmed that the mass ratio of NC and TiN was nearly 3:5.

In order to ascertain the origin of the amorphous carbon, the

45 annealed samples of SiC with melamine (Sample 1) and TiO₂ with melamine (Sample 2) were also prepared at the same process (1000°C, 3h, N₂) in comparison with NC-TiN/SiC. The Raman spectra (Fig. S3 in ESI) showed that no amorphous carbon was presented in Samples 1 and 2. While sp² carbons were present in

50 Sample 3 which was obtained only by annealing the TiO₂/SiC without addition of melamine. It implied that TiO₂ nanoparticles may promote the 'graphitization' of SiC surface which was known to occur at high temperature (>1300°C) under vacuum or inert atmosphere because of evaporation of Si atoms.[16] And the

55 surface carbon layer derived from SiC was doped with N atoms simultaneously with nitridation of TiO₂.

The ORR catalytic activity of NC-TiN/SiC was investigated by the linear sweep voltammeter (LSV) measurements on a rotating disk electrode (RDE). Fig. 3a displays the LSV curves on the SiC,

60 TiO₂/SiC, NC-TiN/SiC and Pt/C (20 wt% Pt supported on Vulcan XC-72, preparation details see ESI) catalysts in O₂-saturated 0.1 M KOH at 1600 rpm. A relatively flat current plateau and higher

limiting current density were observed on the LSV curve of the NC-TiN/SiC in comparison with SiC and TiO$_2$/SiC. The half-wave potential (E$_{1/2}$) of NC-TiN/SiC was 0.82 V (vs. RHE), approached to Pt/C (0.86 V) although the limiting current density of NC-TiN/SiC was slightly lower than Pt/C. The value of E$_{1/2}$ for reported commercial Pt/C[17] was 0.84 V, only 20mV positive shift compared with NC-TiN/SiC, suggesting the excellent ORR catalytic activities of NC-TiN/SiC. Compared with only NC on SiC reported in literature,[18] the NC-TiN/SiC exhibited higher ORR activity, which may be attributed to a synergistic effect of TiN and NC.

LSV curves of the NC-TiN/SiC electrocatalysts in Fig. 3b were obtained at various rotation speeds on RDE, and the currents were normalized by the geometric area of the electrode. Based on it, the Koutecky-Levich (K-L) plots at 0.35 V was obtained, which was shown in the inset of Fig. 3b. It showed a good linear dependence between the reciprocal of current (j^{-1}) and the reciprocal of the square root of the rotation frequency ($\omega^{-1/2}$). The electron transfer number per oxygen molecule involved in the ORR process was determined by the K-L equations:

$$\frac{1}{j} + \frac{1}{j_k} + \frac{1}{B\omega^{1/2}} \tag{1}$$

Where j and j_k are the measured current density and the kinetically current density (mA cm^{-2}), respectively; ω is the angular rotation frequency (rad s^{-1}); B is Levich constant which can be obtained from the slope of the K-L plot.[19] The electron transfer number of SiC, TiO$_2$/SiC and Pt/C obtained from the LSVs (Fig. S4 in ESI) were 2.6, 3.0 and 3.94 at 0.35 V, respectively, while that of NC-TiN/SiC was 3.9, indicating a close four-electron transfer mechanism for ORR on the NC-TiN/SiC electrocatalyst.

The durability of NC-TiN/SiC and Pt/C catalysts toward ORR was evaluated through I-T measurements at 0.75 V in O$_2$-saturated 0.1 M KOH solutions at 1600 rpm, which are shown in Fig. 3c. After 8000s test, the NC-TiN/SiC catalyst remained 95.1% of its original current with a slight activity loss, whereas Pt/C (20 wt%) remained only 81.2% and the reported commercial Pt/C (20 wt%) remained nearly 84% after 8000s[17]. This indicated a much better stability of NC-TiN/SiC catalyst than commercial Pt/C in alkaline solution. An accelerated durability (ADT) test was also conducted from -0.1 to 1.2 V for 3000 cycles. The area in CV curves and the onset potential in LSV curves (Fig. S5 in ESI) of NC-TiN/SiC almost didn't change after ADT, indicating a good oxidation resistance of NC-TiN/SiC. The high stability of the NC-TiN/SiC was mainly ascribed to the unique hybrid structure: highly stable SiC particles covered with TiN nanoparticles and NC layer which not only promoted the catalytic activity of ORR in harmony with TiN but also anchored TiN particles to avoid the TiN agglomeration.

For direct methanol fuel cells—a sub-family of PEMFCs，it is quite needed for an ORR catalyst against the oxidation of methanol crossing from anode to cathode. The methanol resistance was measured by chronoamperometric (CA) measurements in O$_2$-saturated 0.1 M KOH solution followed by addition of 3 M methanol at 750 s. In Fig. 3d, the NC-TiN/SiC retained stable current response after the addition of methanol, in contrast, the Pt/C showed a sharp current increase instantaneously, indicating the ORR activities of NC-TiN/SiC were not influenced by methanol. The same conclusion was also obtained from the CV results. No oxidation peak was observed in the CV curve of NC-TiN/SiC in O$_2$-saturated 0.1 M KOH solution containing 3 M methanol, whereas the Pt/C showed clear methanol oxidation peaks (Fig. S6 in ESI). All these showed that NC-TiN/SiC had an excellent methanol tolerance.

In summary, we synthesized a novel NC-TiN/SiC hybrid by a simple two-step method, in which anatase TiO$_2$ was deposited on the surface of SiC to obtain TiO$_2$/SiC followed by heating a mixture of TiO$_2$/SiC and melamine at 1000°C in N$_2$ protective atmosphere. A hybrid structure with SiC particles covered by TiN nanoparticles and NC layer was obtained. The NC-TiN/SiC electrocatalysts exhibited comparable ORR catalytic activities as traditional Pt/C, as well as superior stability and methanol tolerance. The outstanding catalytic performances were ascribed to the synergistic effect of TiN and NC and the unique hybrid structure. NC-TiN/SiC was proved to be a promising catalyst for ORR due to its excellent ORR activities, high stability and strong methanol resistance.

Notes and references

a State Key Laboratory of Metastable Materials Science and Technology, College of Materials Science and Engineering, Yanshan University, Qinhuangdao 066004, PR China. Fax: +86–335–8387679; Tel: +86–13930308747; E-mail: diamondzjb@163.com

† Electronic Supplementary Information (ESI) available: Experimental Details, X-ray diffraction, Roman and partly electrocatalytic results. See DOI: 10.1039/b000000x/

1   I.E.L. Stephens, A.S. Bondarenko, U. Grønbjerg, J. Rossmeisl, I. Chorkendorff, *Energy Environ. Sci.*, 2012, **5**, 6744
2   V.D.Noto, E.Negro, S.Polizzi, K.Vezzu, L.Toniolo,G.Cavinato, *Int. J. Hydrogen Energy*, 2014, **39**, 2812
3   V.D.Noto, E.Negro, S.Polizzi, F.Agresti, G.A.Giffin, *ChemSusChem.*, 2012, **5**,2451
4   N.A. Karim, S.K. Kamarudin, *Appl. Energy*, 2013, **103**, 212
5   J. Zhang, A. Byeon, J.W. Lee, *Chem.Commun.*,2014,**50**,6349
6   R.B. Valim, M.C. Santos, M.R.V. Lanza, S.A.S. Machado, F.H.B. Lima, M.L. Calegaro, *Electrochim. Acta* 2012, **85**,243
7   S. Shanmugam, T. Osaka, *Chem. Commun .*, 2011, **47**, 4463
8   S.Dou, A.Shen, T. Tao, S.Y. Wang, *Chem. Commun.*,2014,**50**,10672
9   Y.Y. Shao, J.H. Sui, G.P. Yin, Y.Z. Gao, *Appl. Catal., B* 2008,**79**,89
10   D.H. Youn, G.H. Bae, S.Han, J.Y. Kim, J.W.Jang, H. Park, S.H.Choi, J.S. Lee, *J.Mater. Chem. A* 2013, **1**, 8007
11   J.Chen, K.Takanabe, R.Ohnishi, D.Lu, S.Okada, H.Hatasawa, H. Morioa, M.Antonietti, J.Kubota, K.Domen, *Chem.Commun.*, 2010,**46**, 7492
12   M.Liu, Y.Dong, Y.Wu, H. Feng, J.Li, *Chem. Eur. J.* 2013, **19**, 14781
13   H. Lv, S. Mu, N.Cheng, M. Pan, *Appl. Catal.,B*, 2010,**100**,190
14   J. Huang, J. Zang, Y. Zhao, L. Dong, Y.Wang, *Mater. Lett.,* 2014, **137**, 335
15   M. Chisaka, H. Muramoto, *ChemElectroChem*, 2014,**1**,544
16   J. Zang, L. Dong, Y. Jia, H. Pan, Z.Gao, Y.Wang, *Appl.Catal.,B*, 2014, **144**, 166
17   Y.Tan, C.Xu, G.Chen, X.Fang, N.Zheng, Q.Xie, *Adv. Funct. Mater.*, 2012, **22**, 4584
18   H.Pan, J.Zang, X.Li, Y.Wang, *carbon,* 2014, **69,** 630
19   X. Li, G. Liu, B.N. Popov, *J. Power Sources*, 2010,**195**,6373