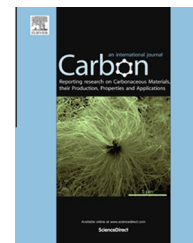


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Letter to the Editor

One-pot synthesis of shell/core structural N-doped carbide-derived carbon/SiC particles as electrocatalysts for oxygen reduction reaction



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ARTICLE INFO

Article history:

Received 11 September 2013

Accepted 9 December 2013

Available online 12 December 2013

ABSTRACT

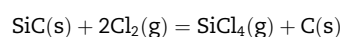
An N-doped carbide-derived carbon shell was in situ derived from the surface of SiC nanoparticle by a one-pot method. Characterizations and electrochemistry experiments demonstrate that the prepared particles have a shell/core structure and exhibit a four-electron transfer pathway for oxygen reduction reaction as well as a superior stability compared with Pt/C catalysts.

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One of the urgently required researches for promoting commercialization of fuel cells is to explore more effective and stable non-Pt electrocatalysts for replacing the high costly Pt-based catalysts. N-doped carbon nanostructures have been intensively studied because of their high electronic conductivity, electrocatalytic activity, tolerance to crossover effect and low cost [1]. However, the insufficient durability of most synthesized N-doped carbon nanostructures is a critical issue unsolved.

Here we report an N-doped carbide-derived carbon (N-CDC) material, which is in situ derived from SiC nanoparticle. CDCs are usually produced by selective etching of carbides in halogens (such as Cl_2) [2,3]. In this work, a new method is adopted to synthesize a shell/core structural N-CDC/SiC material, in which the surface of nano-SiC is converted to N-doped CDC shell and the SiC core is retained. The SiC core can retain high thermal and morphological stability and the N-CDC shell can provide the catalyst an excellent catalytic performance for oxygen reduction reaction (ORR) [4]. Therefore the N-CDC/SiC is expected to be a good candidate for cathode catalyst in Fuel cells. N-CDC shell forms during the process of vacuum annealing the mixture of SiC, NiCl_2

and melamine at 1000 °C, under which NiCl_2 decomposes into Cl_2 and Ni. Cl_2 can extract Si atoms from SiC by the following reaction:



In addition, Ni can facilitate incorporating N atoms into carbon shell and forming larger proportion of edge plane exposure, which is one of the accounts for the excellent ORR activity [5,6].

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were carried out before and after annealing. The pristine SiC presents sphere-like particles with an average size of 60 nm (Fig. 1a). Its HRTEM image (Fig. 1b) shows 0.252 nm lattice fringes corresponded to the (111) planes of 3C-SiC. The flat surface becomes rough after annealing (Fig. 1c). The HRTEM image in Fig. 1d shows an amorphous carbon shell on SiC. D and G bands which are characteristic peaks of graphitic carbons appear in the Raman spectrum (Fig. S1 in Supplementary material), confirming the formation of CDC shell. The corresponding electron energy loss spectroscopy (EELS) result at right upper of Fig. 1d displays two obvious peaks located at 283 and 403 eV

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<http://dx.doi.org/10.1016/j.carbon.2013.12.022>

corresponding to the C and N peaks, respectively, indicating that N dopants present in the CDC shell. The decomposed Cl_2 from NiCl_2 selectively removed Si atoms from SiC substrate and transformed the surface carbide structure into CDC shell. Simultaneously, Ni served as an accelerant, which facilitated the incorporation of N and formed doped carbon materials with a greater proportion of edge plane exposure.

In order to demonstrate the effect of NiCl_2 , we tried to synthesize N-doped C shell on SiC only using SiC and melamine under the same conditions. The TEM results show almost no morphology change on SiC. Moreover, the sample shows no catalytic activity improvement for ORR (Fig. S2), implying that N-doping C shell has not formed without NiCl_2 .

X-ray photoelectron spectroscopy (XPS) measurement was carried out to analyze the elemental composition and the chemical bonding environment of doped N atoms. The survey scan spectrum (Fig. 2a) reveals the presence of principal Si, C, N and O, further demonstrating the successful incorporation of N with a nominal level of 5.9 atom%. The presence of O can be attributed to the oxidized carbons, which was produced by the Ni removal process in strong oxidizing acid. The high-resolution N1s spectrum (Fig. 2b) is deconvoluted into several individual peaks at 397.2, 399.2, 400.4 and 402.4 eV corresponding to tetrahedral N, pyridinic N, pyrrolic N, and graphitic N, respectively. Tetrahedral N bonds to the

sp^3 C due to the unparted N–H bond in the melamine precursor [7]. Pyridinic N and graphitic N, which are both sp^2 hybridized, play an important role in enhancing the ORR activity [8].

Linear sweeping voltammograms (LSVs) in O_2 saturated 0.1 M KOH at a scan rate of 10 mV s^{-1} were recorded to explain the electrocatalytic activity of N-CDC/SiC particles toward ORR (Fig. 3a). For comparison, LSVs (Fig. 3d) of the undoped CDC/SiC particles and commercial 20 wt% Pt/C catalysts (Pt electrocatalysts supported on Vulcan XC-72) were also measured under the same conditions (details are given in Supplementary Material). N-CDC/SiC particles have a lower catalytic activity than Pt/C catalysts, but higher than CDC/SiC. From the K–L plots of N-CDC/SiC (Fig. 3b), it can be calculated that the electron transfer number (n) for N-CDC/SiC particles is about 3.886 at potential range from -0.2 V to -0.6 V , indicating that the reduction of O_2 is almost a four-electron process. In contrast, the CDC/SiC particles typically show a two-electron transfer pathway for ORR (Fig. S3). The calculated Tafel slope value for N-CDC/SiC particles at the mixed controlled region from -0.06 V to -0.015 V (Fig. 3c) is $-56.1 \text{ mV dec}^{-1}$, which is close to that of Pt in alkaline media (60 mV dec^{-1}), indicating that the N-CDC/SiC particles exhibit a good ORR kinetics [9,10].

The stability of the electrocatalyst is one of the key factors that affect the durability and reliability of fuel cells. In this

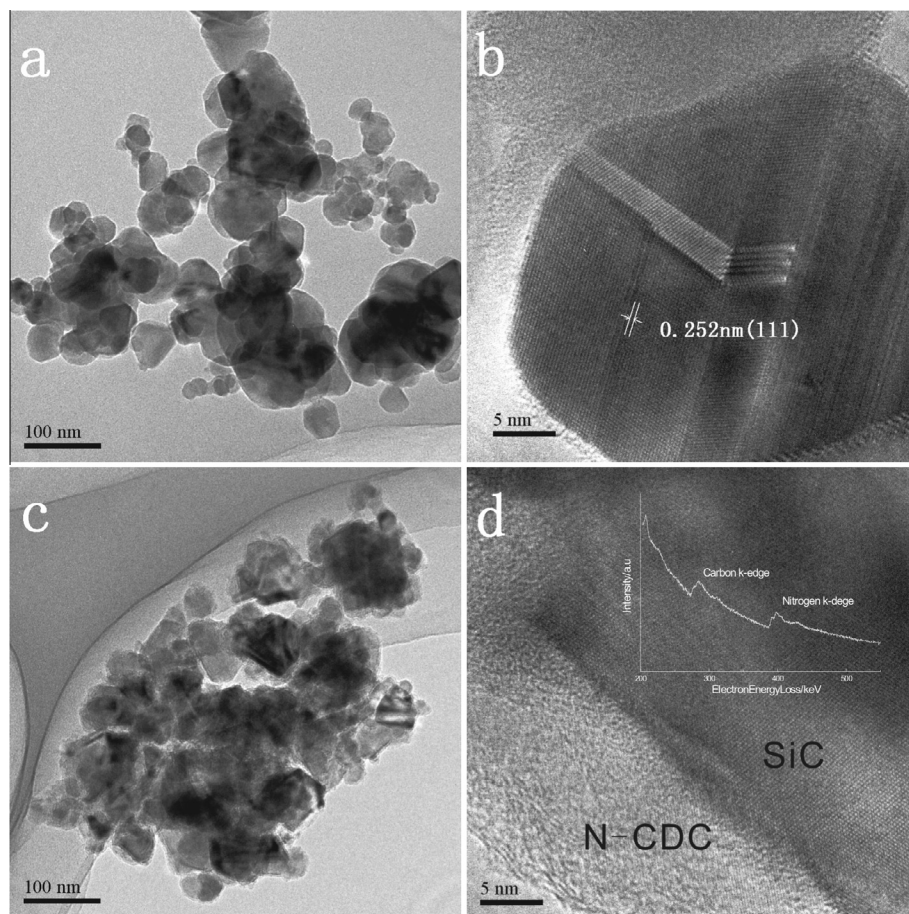


Fig. 1 – (a) TEM image of pristine SiC particles. (b) HRTEM image of pristine SiC particle. (c) TEM image of N-CDC/SiC particles. (d) HRTEM image of N-CDC/SiC particles, inset: EELS result of N-CDC/SiC particles.

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