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Short communication

Synthesis of shell/core structural nitrogen-doped carbon/silicon carbide and its electrochemical properties as a cathode catalyst for fuel cells

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ABSTRACT

A shell/core structural N-doped carbon/silicon carbide (N-doped C/SiC) was prepared by two-steps: pre-carbonization and N doping process. The first step was carried out on nano-SiC using acid etching method. Nanoporous amorphous carbons were formed on the surface of SiC after acid etching, which could make it easy to adsorb N source and reduce the energy needed in the next step. The prepared N-doped C/SiC exhibited a high durability and a good catalytic activity for oxygen reduction reaction.

1. Introduction

The carbon-supported platinum (Pt) electrocatalysts are currently accepted catalyst materials for oxygen reduction reaction (ORR) in polymer electrolyte membrane fuel cells (PEMFCs). However the issues of (i) the heavy consumption of noble metals which are finite natural resource materials, (ii) the insufficient durability and (iii) the crossover of methanol from anode into the cathode side have become a technological bottleneck for the industrial development of PEMFCs [1]. Therefore, it is urgently required to explore effective and stable Pt-free electrocatalysts to replace Pt-based catalysts. Nitrogen (N)-doped carbon nanostructures, such as N-doped carbon nanotubes and N-doped graphene, have been receiving lots of attentions as non-noble-metal electrocatalysts [2–7]. It was reported that N doping can greatly improve the ORR activity of carbon materials although the ORR mechanism is still unclear [8–11]. However most synthesized N-doped carbon materials reported are based on sp^2-bonded carbon structures, which inevitably suffer from the corrosion caused by high potential, moisture and perhaps hydrogen peroxide in typical cathode conditions. The serious catalyst corrosions even cause catastrophic electrode failure. Therefore, the synthesis of N-doped carbon electrocatalyst materials with a high stability is much required.

Here we report a novel shell/core structural N-doped carbon/silicon carbide (N-doped C/SiC) with a nanoscale SiC core covered by an N-doped carbon shell. Compared with the commonly used sp^2-bonded carbon materials, the sp^3-bonded SiC is highly resistant to electrochemical corrosion [12]. First, a controlled nanoporous amorphous carbon layer was in-situ derived from SiC by acid etching, which makes it easy for the incorporation of N. And then a vacuum annealing treatment on the mixture of pre-carbonized SiC and N source (melamine) was conducted at 1300 °C and 10^{-3} Pa for doping N into the carbon layer. The prepared shell/core structural N-doped C/SiC is expected to be a good candidate for cathode catalyst for fuel cells because the SiC core retains high thermal and morphological stability and the N-doped carbon shell endows it an excellent catalytic performance for ORR.

2. Experimental methods

Nanocrystalline 3C-SiC powder with an average particle size of 60 nm was purchased from Hefei Kaier Nano-Power Technology Inc., China. All reagents such as hydrofluoric acid (HF), nitric acid (HNO_3), potassium hydroxide (KOH) and methanol were analytical grade. Deionized water was used throughout the experiments.

First, SiC powders were etched by the mixed acids of HF and HNO_3 at room temperature for 24 h. After rinsed, the powders were annealed with melamine at 1300 °C in 10^{-3} Pa vacuum for 3 h. Then the prepared powders went through a cooling down process in N_2 protective atmosphere. As a contrast, undoped C/SiC was also synthesized under the same process except for melamine additions.

The morphologies of the synthesized samples were characterized by high resolution transmission electron microscopy (HRTEM) (JEOL, JEM2010) equipped with electron energy loss spectroscopy (EELS) at 200 kV. Raman analysis was performed by a Renishaw inVia Raman microscope using the 514 nm line from an Ar ion laser. X-ray photoelectron spectroscopy (Perkin-Elmer PHI5300) was carried out using a monochromatic Al K_α X-ray source.

Cyclic voltammetry (CV), linear sweep voltammetry (LSV) and current–time (I–T) measurements were performed on a rotating disk electrode (RDE) with a typical three-electrode cell using an

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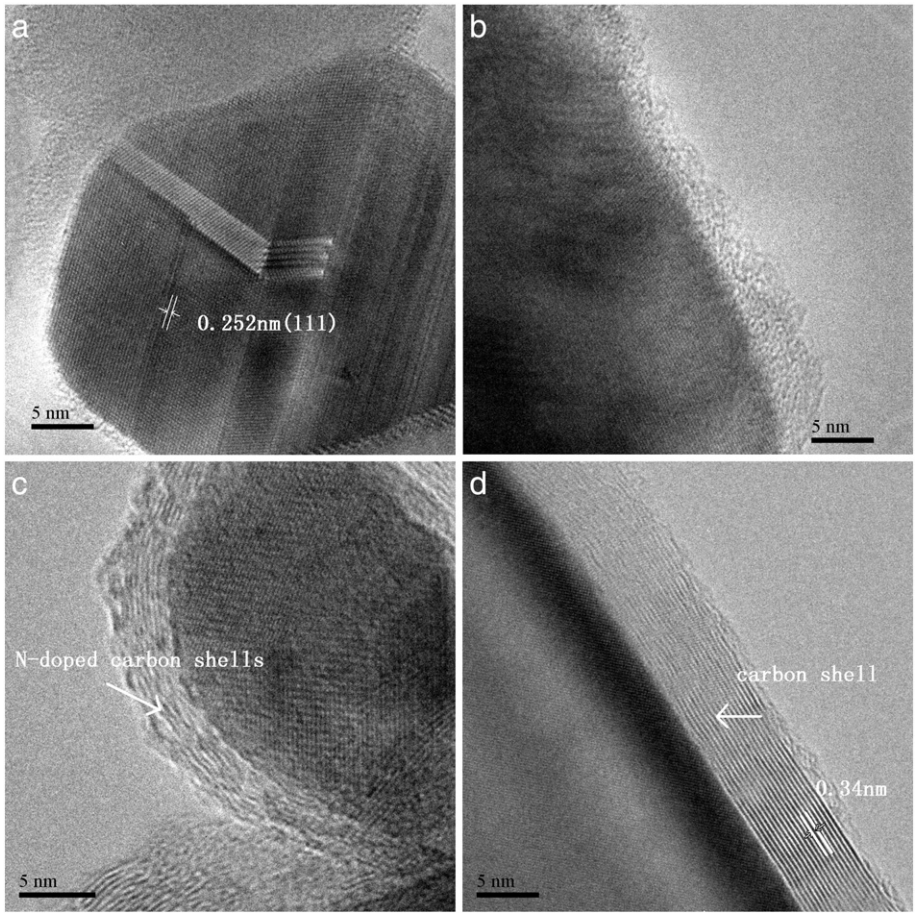

Fig. 1. HRTEM images of (a) pristine SiC, (b) acid etched SiC, (c) undoped C/SiC and (d) N-doped C/SiC.

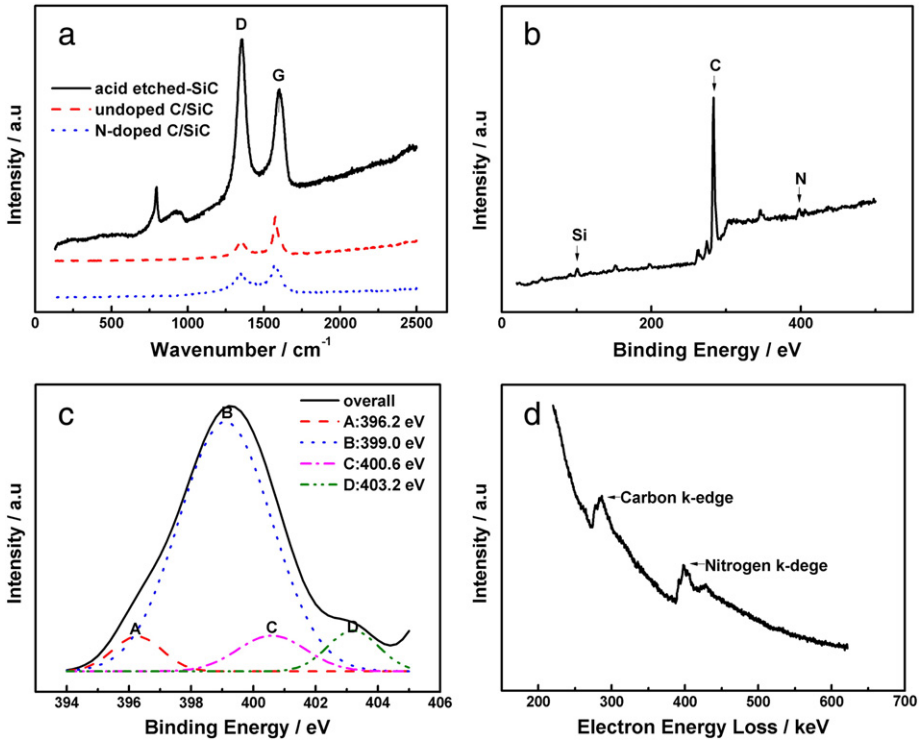

Fig. 2. (a) Raman spectra of acid etched SiC, undoped C/SiC and N-doped C/SiC. (b) XPS spectrum of N-doped C/SiC. (c) High-resolution N1s peaks of N-doped C/SiC. (d) EELS result of N-doped C/SiC.