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# Chlorine effect on formation of turbostratic carbon nanofibers by a mixture of 1,2-dichloroethane and ethanol

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ABSTRACT

Turbostratic carbon nanofibers (TSCNFs) were synthesized by the pyrolysis of a 1,2-dichloroethane (DCE)/ethanol mixture in the presence of Ni catalyst at 700 °C. The TSCNFs were formed by the random stacking of short and disordered graphene sheets that became porous and string-like fibers with diameters in the range of 50–100 nm. The participation of chlorine was found to play an important role in the synthesis of the TSCNFs. Auger electron spectrometry analysis and electron microscope observations reveal that Ni–Cl bonding on the surface of the catalysts creates a relatively poor crystalline layer, leading to a coarse surface. The coarse surface causes the disordered precipitation of carbon species (graphene) from the catalyst surface and thus the formation of TSCNFs. TSCNFs formed when the concentration of DCE in the mixture was more than 20 vol%. In addition, the electrochemical properties of TSCNFs were studied. The specific capacitance of the TSCNFs prepared by the pyrolysis of DCE was 62.7 F/g in 1 M $H_2SO_4$ at 2 mV/s.



## 1. Introduction

Fibrous carbon nanomaterials with a porous structure such as porous carbon nanofibers (CNFs) [1–4] and activated CNFs [5,6] have attracted a lot of attention due to their unique crystalline structure as well as excellent physical and chemical properties. A wide variety of applications, such as electrode materials [1–5,7,8], catalyst supports [6,9], adsorbents [10,11], and gas storage [12,13], have been reported.

CNFs are synthesized mainly using catalytic chemical vapor deposition (CCVD) [14–19]. CCVD is an efficient method for production as it allows the control of synthesis parameters such as reaction temperature, carbon source, and type of catalyst. The decomposition of a carbon source (CO, $CH_4$, or $C_2H_2$) on catalysts (Fe, Co, Ni, or their alloys) allows a solid solution of metal carbides to form. Excess carbon atoms in the metal carbide diffuse out from the catalyst to form CNFs. In several recent reports, ethanol was found to be an attractive precursor for the synthesis of carbon nanotubes (CNTs) and CNFs. Pan et al. [20] synthesized CNTs using an ethanol flame. Maruyama et al. [21,22] fabricated single-walled CNTs from ethanol vapor at relatively low temperatures and reduced pressures. Red'kin et al. [23] reported that ethanol molecules decompose into simpler species, such as $CH_4$, CO, and $H_2$, which grow into CNFs of various thicknesses or CNTs on Ni catalysts. Bao et al. [24] synthesized CNFs at atmospheric pressure by the ultrasonic spray pyrolysis of ethanol without a catalyst.

The morphology of CNFs strongly depends on the shape of the catalyst, which is greatly affected by process temperature [14,25,26]. Several types of CNF, such as turbostratic CNFs (TSCNFs), platelet graphite nanofibers (PGNFs), tubular GNFs, and tapered CNTs, have been formed by the polymer pyrolysis method using $NiCl_2$ as catalyst at temperatures ranging from 600 to 800 °C [26–31]. In addition to the effect of temperature, the participation of halide in the synthesis changes the properties of catalysts, which determine the types of CNF formed. The properties include the melting point, morphology, particle size, and geometrical shape of the catalyst [16,32,33].

In this study, the TSCNFs were synthesized by the pyrolysis of a mixture of ethanol and 1,2-dichloroethane (DCE) in the presence of Ni as the catalyst. The mixture affects the shape of the catalyst and the types of TSCNF formed. Characterizations of the formed TSCNFs were conducted in order to investigate the interaction between chlorine, Ni catalyst, and TSCNFs. In addition, the electrochemical properties of the TSCNFs were studied.

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## 2. Experimental details

### 2.1. Preparation of TSCNFs

TSCNFs were formed by the decomposition of an ethanol and DCE (purity 99.99%, ECHO) mixture in the presence of Ni catalyst. The catalyst was prepared as follows. 0.5 M nickel(II) acetate (purity 99%, Showa) as the Ni catalyst precursor and 0.5 M monoethanolamine (purity 99.7%, J.T. Baker) were dissolved and well mixed in 2-methoxyethanol (purity 99%, Alfa Aesar) at 60 °C until the color of the solution became translucent green. The solution was spin-coated onto a silicon chip, which was then thermally treated at 700 °C for 30 min in air. For TSCNF synthesis, the as-prepared chip was placed in the middle of a tubular furnace. $N_2$ gas was admitted into the quartz reactor while the furnace was heated from room temperature to 600–800 °C at a rate of 15 °C/min. Mixtures of DCE and ethanol with various ratios (0–100 (v/v)) were prepared in a round-bottom flask, which allowed carrier gas to be delivered. Once the reactor reached the desired temperature, 100 sccm of $H_2$ was introduced for the reduction of the catalyst. After 10 min of the reduction process, the mixture was carried by 100 sccm of $H_2$ introduced into the quartz tube for 20 min for the synthesis of TSCNFs. A schematic of the apparatus is shown in Fig. 1.

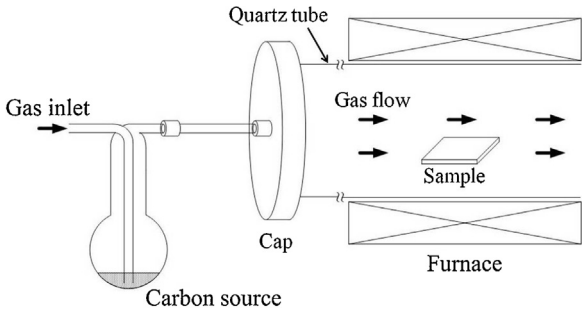


**Fig. 1.** Schematic of apparatus used for TSCNF synthesis.

The morphology of the TSCNFs was observed using field-emission scanning electron microscopy (SEM, Hitachi S-4800) and the crystal structure was examined using transmission electron microscopy (TEM, FEI Tecnai F20). A Raman scattering spectrometer (Horiba XploRA) was used to determine the relative intensities of the G-band and D-band. The thermal stability of the CNFs was analyzed using thermal gravimetric analysis (TGA, PerkinElmer Diamond TG/DTA). Approximately 2 mg of the material was heated in an alumina pan at a rate of 10 °C/min to 800 °C under an air atmosphere. The surface area of TSCNFs was measured by nitrogen adsorption–desorption isotherms at 77 K (Micrometric ASAP 2010). The qualitative analysis of elements on the specimen surface was conducted by auger electron spectrometry (AES, ULVAC-PHI PHI 700).

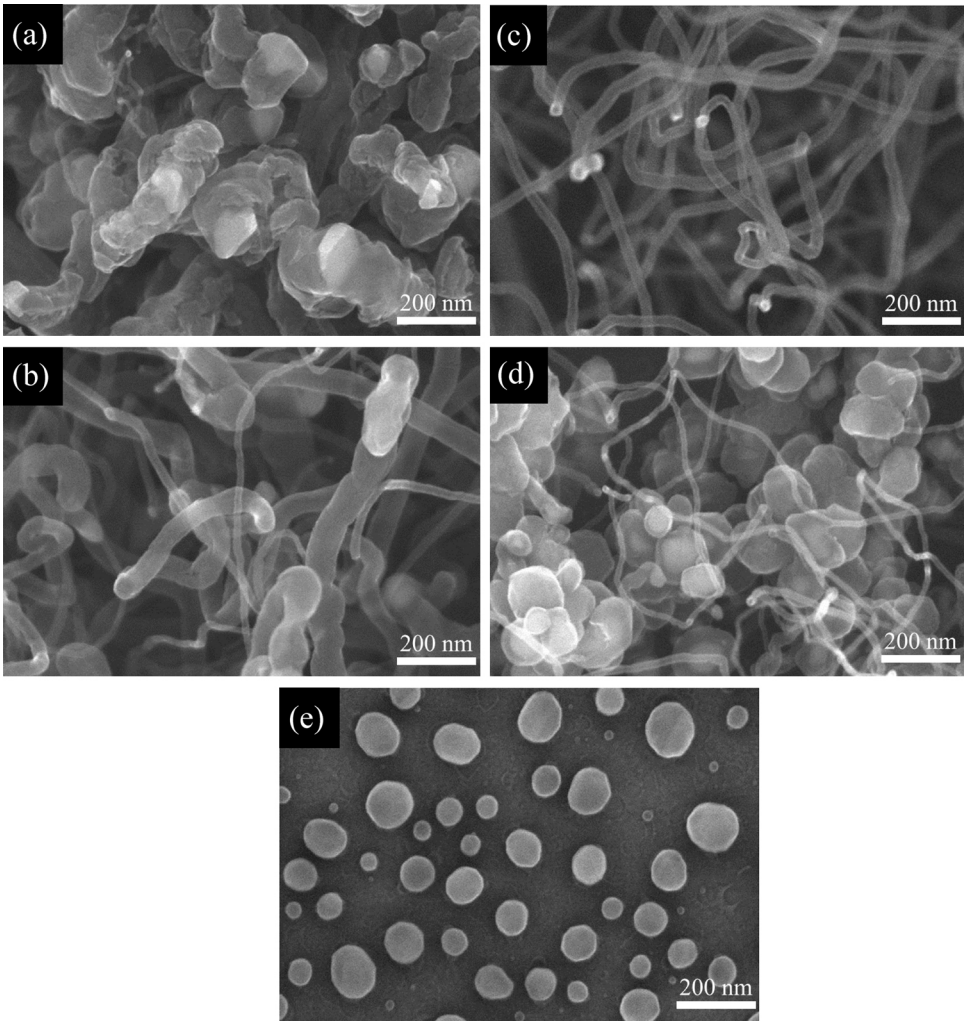


**Fig. 2.** SEM images of temperature effect on materials synthesized using ethanol as carbon source at (a) 600, (b) 650, (c) 700, (d) 750, and (e) 800 °C.

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