

Helical nanocoiled and microcoiled carbon fibers as effective catalyst supports for electrooxidation of methanol

Lu Zhang, Feng Li*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, No. 15, Bei Sanhuan Donglu, P.O. Box 98, Beijing 100029, PR China

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ABSTRACT

We have demonstrated a new synthesis of twist-shaped nanocoiled and herringbone-type double microcoiled carbon fibers via catalytic chemical vapor deposition of acetylene over NiCuMgAl-layered double hydroxides. The materials were characterized by power X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and N₂ adsorption–desorption experiments. For the first time, the use of electrodes modified with platinum particles supported on as-grown helical carbon fibers was studied for electrocatalytic oxidation of methanol. Especially, the electrode supported on herringbone-type double microcoiled carbon fiber showed much larger Pt active surface area than that supported on commercial carbon black. Furthermore, such electrocatalyst has exhibited about fourfold enhancement of activity and excellent anti-poisoning ability, which is believed to be attributed to the combined beneficial effects of novel microstructure and special composition of as-grown helical carbon fibers.

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1. Introduction

One-dimensional (1D) carbon materials have attracted increasing attention because of their potential applications in a variety of fields including composites, field emission, nanoelectronics, hydrogen storage, capacitors, electrodes, adsorbents and nanosensor materials [1–3], owing to their distinct physico-chemical properties, such as high resistance to strong acids and bases, high mechanical strength, superior adsorption capabilities, high tensile modulus and high electric conductivities. In particular, in developing the high performance electrocatalysts of direct alcohol fuel cells (DAFCs), the use of 1D carbon materials as support could enhance the electrocatalytic activity of alcohol oxidation, which is closely related to their geometrical microstructure and desirable hosting structure for noble metal catalyst particles [4–6], as well as high protection ability for carbon monoxide poisoning [7–9]. However, in recent years, few works have been carried out on carbon nanofibers (CNFs) as fuel cell electrocatalyst support, but tests in DAFC systems of CNFs showed promising results [7,10,11]. The morphology and microstructure of carbon-based support materials, however, have great impact on their electrochemical properties. Accordingly, in terms of the design and application of an excellent catalyst support in DAFCs, preparation of carbon materials with novel crystallographic microstructure for good conductivity and interaction between

catalyst particles and the support represents an attractive goal [11].

Recently, we found that CNTs and CNFs could be synthesized by the high temperature catalytic chemical vapor deposition (CCVD) of acetylene over highly active cobalt- and nickel-based supported catalysts derived from layered double hydroxides (LDHs) [12–14]. LDHs, known as a family of synthetic anionic clays, are a class of brucite-like layered materials [15]. They can be expressed by the general formula $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^{2+} (Mg^{2+} , Ni^{2+} , Co^{2+} , Cu^{2+} or Zn^{2+}) and M^{3+} (Al^{3+} , Fe^{3+} , Cr^{3+} or Ga^{3+}) are divalent and trivalent cations coordinated tetrahedrally or octahedrally with hydroxyl groups to form infinite two-dimensional layers by edge-sharing, and anions (A^{n-}) are intercalated into the interlayer by electrostatic interactions with positively charged layers. The structural versatility of LDHs has been achieved by varying divalent or trivalent metal cations in the layers and the anions intercalated into the interlamellar galleries [16–18]. These materials are potential precursors for metal catalyst in virtue of their layer structure and adjustable components. Thus, highly dispersed metal nanoparticles on metal oxide matrix can be obtained by designing appropriate LDHs containing desired metal cations and subsequent thermal treatment followed by reduction.

In the present work, we demonstrated a new synthesis of twist-shaped nanocoiled and herringbone-type double microcoiled carbon fibers via CCVD of acetylene over LDHs containing Ni^{2+} , Cu^{2+} , Mg^{2+} and Al^{3+} cations. The electrodes modified with platinum particles supported on as-grown helical carbon fibers showed superior electrocatalytic activities and stabilities for the electrooxidation of methanol to that supported on commercial carbon black.

* Corresponding author. Tel.: +86 10 64451226; fax: +86 10 64425385.
E-mail address: lifeng_70@163.com (F. Li).

To the best of our knowledge, the study of the electrochemical performance of helical nanocoiled and microcoiled carbon fibers as support in electrooxidation of alcohols has not been reported before.

2. Experimental

2.1. Preparation of materials

LDHs containing M^{2+} and Al^{3+} cations ($M^{2+} = Ni^{2+}$, Cu^{2+} and Mg^{2+}) were synthesized under hydrothermal conditions through homogenous decomposition of urea. In a typical synthesis, urea, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 7H_2O$ with the $(Ni^{2+} + Cu^{2+} + Mg^{2+})/Al^{3+}$ molar ratio of 3.0 and different $Ni^{2+}/Cu^{2+}/Mg^{2+}/Al^{3+}$ molar ratios (2.7:0.3:0:1 and 2.7:0.3:6:3, respectively) were dissolved in 80 mL of deionized water to present a clear solution with the total cation concentration of 0.05 M. Here, the molar ratio of urea to total metal cations is 3.3. Then the aqueous solution was transferred to 100 mL of Teflon-lined autoclave and heated at 150 °C for 24 h. The suspension was washed with deionized water for four times, and the obtained solid was dried at 70 °C for 12 h in air. The as-synthesized Mg-free LDH sample is denoted as LDH-1 and another LDH sample is denoted as LDH-2.

Carbon materials were in situ prepared in a quartz tube with the diameter of 50 mm inside a horizontal tube furnace equipped with mass controller and temperature-programmed control by CCVD of acetylene. After loading the LDH sample in an alumina boat, the furnace was first raised to 700 °C with 5 °C/min under nitrogen gas flow (flow rate: 60 standard-state $cm^3 \text{ min}^{-1}$ (sccm)) for 30 min. Subsequently, C_2H_2 gas was switched into the furnace with a flow rate of 6 sccm, and the furnace temperature was maintained at 700 °C for 90 min. After the reaction, N_2 gas was continued till the furnace was cooled to room temperature. The resultant black powder was collected from the boat.

The working electrode for methanol and ethanol oxidation was first fabricated by casting 10% polytetrafluoroethylene (PTFE)-impregnated carbon material supports onto carbon paper with the surface area of 0.5 cm^2 . Then, working electrode modified by Pt particles was synthesized at room temperature by electrodeposition from an aqueous solution containing 0.005 M H_2PtCl_6 and 0.5 M H_2SO_4 at -0.2 to 0.6 V vs SCE for 1800 s. The amount of Pt deposited on the support was calculated from the charge consumed during the electrodeposition of Pt using Faraday's law according to the faradic reaction ($PtCl_6^{2-} + 4e \rightarrow Pt + 6Cl^-$). Under the identical deposition conditions, the amount of Pt deposited on carbon support can change with the microstructure of supports. For comparison, the electrode modified with Pt supported on a commercial Vulcan XC-72 carbon black purchased from Cabot Co. (USA), denoted as Pt/C electrode, was also prepared using the identical method.

2.2. Characterization

Powder X-ray diffraction (XRD) pattern of samples were collected using a Shimadzu XRD-6000 diffractometer under graphite-filtered $Cu \text{ K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$).

Scanning electron microscopy (SEM) analyses of the samples were made using a Hitachi S4700 apparatus with the applied voltage of 20 kV. Transmission electron microscopy (TEM) images were taken using Philips FEI TECNAI 20 transmission electron microscope operated at 120 kV. Energy dispersive X-ray spectrometer (EDX) was employed to analyze chemical composition.

Raman spectra were recorded at room temperature on a microscopic confocal Raman spectrometer (Jobin Yvon Horiba

HR800) using an Ar^+ laser of 532 nm wavelength as excitation source.

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a V.G. Scientific ESCALAB Mark II system and $Mg \text{ K}\alpha$ ($h\nu = 1253.6 \text{ eV}$) as X-ray source. The binding energies (BE) were referenced to the C1s peak at 284.6 eV. The experimental curve was fitted with a program that made use of a combination of Gaussian–Lorentzian lines.

The low-temperature N_2 adsorption–desorption experiments were carried out using a Quantachrome Autosorb-1C-VP system. Specific surface areas of samples were calculated from the adsorption isotherm according to the Brunauer–Emmett–Teller (BET) method.

The electrochemical measurements were carried out with CHI660C electrochemical instrument in a standard three electrode cells at 25 °C, adopting saturated calomel electrode (SCE) and platinum wire as the reference electrode and the counter electrode. A thin film electrocatalyst layer with carbon paper substrate is used as working electrode. The acid aqueous solution containing 0.5 M CH_3OH and 0.5 M H_2SO_4 is used as electrolyte solutions. The electrolyte solution was deaerated by high purity nitrogen gas prior to the reaction. Cyclic voltammetry was performed at a rate of 10 mV s^{-1} .

3. Results and discussion

3.1. Characterization of materials

Fig. 1a and b shows the powder XRD patterns of LDH samples. XRD patterns are similar to those typically reported in the literature for hydrotalcite-like materials observed as the main crystalline phase in samples [19], and give characteristic (003), (006) and (009) peaks corresponding to the basal spacing and higher order diffractions. The XRD patterns of carbon products grown over LDHs were displayed in Fig. 1c and d. The peak centered at about 26.0° is indexed to (002) reflection plane of graphite, confirming the existence of carbon species. Meanwhile, the (111), (200) and (220) reflections of face-centered cubic (fcc) metallic Ni appear. However, as for LDH-1 sample, the appearance of characteristic reflections of

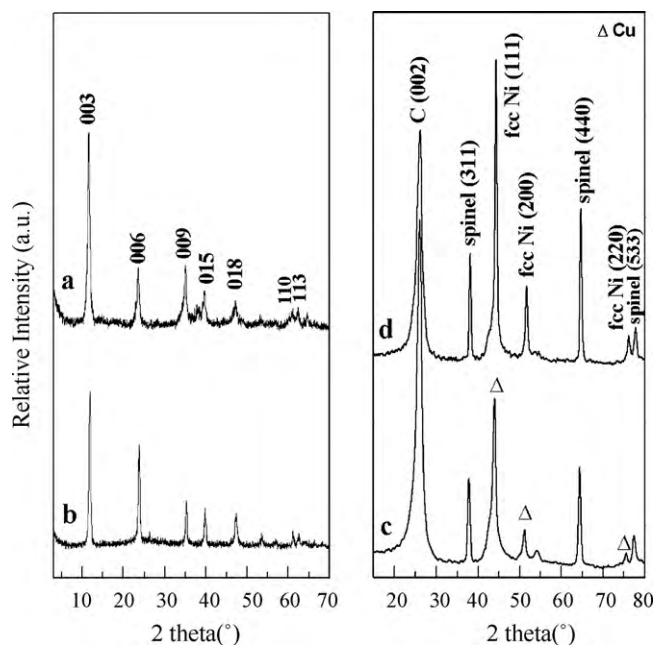


Fig. 1. XRD patterns of LDH samples (a: LDH-1; b: LDH-2) and carbon products grown over LDH samples (c: LDH-1; d: LDH-2).

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