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# Improvement of field-emission-lamp characteristics using nitrogen-doped carbon nanocoils

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ABSTRACT

Carbon nanocoils (CNCs) synthesized using thermal pyrolysis chemical vapor deposition on 304 stainless steel wire substrates were used as the cathodes of field emission lamps (FELs). The effects of the growth temperature on the FE performances were studied, and we observed that uniform and dense CNCs that are suitable for use as FE cathodes can be synthesized at 600 °C. We also found that a nitrogen doping post-treatment can significantly improve the FE efficiency of the CNCs. When doped at 200 °C with a nitrogen flow rate of 500 sccm for 30 min, the nitrogen content of the CNC surface could reach 4.9 wt.%. ESCA analysis indicates that the doped nitrogen atoms formed $CN_x$ bonding and increased the $sp^2$ clusters in the CNCs. The turn-on voltage was reduced from 2.1 V/μm to 1.4 V/μm, and the $\beta$ value increased considerably from 2465 to 3241 after N-doping post-treatment. The bulb-type FELs using our N-doped CNC cathodes showed a good luminous efficiency as high as 75 lm/W at 8 kV.

## 1. Introduction

The phenomenon of field emission (FE) was proposed by Fowler and Nordheim in 1928 [1]. In this phenomenon, electrons can be drawn from high-aspect-ratio or low-work-function cathode materials under a high electric field. This phenomenon is used in a variety of applications such as display panels [2], flat panel displays (for producing backlight) [3], field emission lamps (FELs) [4], and X-ray tubes [5].

FEL devices have numerous advantages such as short switching times, low power consumption, high brightness, and low heat generation; they are also free of mercury. Compared with light-emitting diodes and cold cathode fluorescent lamps, they have an edge as a new-generation, environmentally friendly light source [6]. A literature survey indicated that numerous types of FELs, such as plane-type [7], tube-type [8,9], and bulb-type lamps [10], have been developed.

Because they are characterized by a high aspect ratio and a low turn-on electric field (approximately 0.5–2.9 V/μm) [11–13], carbon nanotubes (CNTs) are used as the cathode material in most FELs that have been recently developed. Hence, the voltage required for operating these FELs is low. However, the use of CNTs leads to problems such as poor lighting uniformity and low light-spot density.

Obraztsov et al. [14–16] reported a new-type of nanocarbon cold cathodes. The nanocarbon thin-film material composed of CNTs and nanosized flake-like graphite crystallites exhibited high homogeneity of field emission site density ($10^6/cm^2$) over the film surface. And a power efficiency of >30% was achieved for the cylindrical diode lamps with the nanocarbon cold cathodes.

The carbon nanocoil (CNC) was first synthesized by Motojima and coworkers [17]; using a nickel substrate or nickel powder as the catalyst, they synthesized microcoiled carbon fibers by using chemical vapor deposition [18]. In 2001, Wen et al. successfully used acetylene as the carbon source and Ni–P–Cl composite catalysts to grow helical CNCs, and they fabricated several CNC structures, including solid and hollow coils [19]. Pan et al. [20] determined that 5-ring or 7-ring carbon bond defects in the nanocoil structure can serve as the FE points (electrons are emitted from these points). Compared with a CNT of the same length, a CNC has considerably more FE points [20,21]. In recent years, several research teams, including the present author's team, have used CNCs as the cathode material to fabricate FEL devices [22,23]. The results of these previous studies have indicated that CNC cathode materials can effectively increase lighting uniformity and light-spot density.

Although the lighting uniformity and light-spot density of CNCs are more favorable compared with those of CNTs, the turn-on electric field of CNCs (typically 1.3–4.5 V/μm) is generally higher than that of CNTs [20,24–27]. In our former works, we found that the CNC cathodes have longer life time than CNT cathodes when ZnS-based phosphors (P22) were used in the anode for its high cathodoluminescent (CL)

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efficiency. It may be explained as follows: for P22, a higher electron kinetic energy, and hence a higher working voltage, is needed to achieve a high CL efficiency, but this will be detrimental for CNT cathodes due to their exceedingly high emission current density at such a high applied voltage and the accompanying coulombic damage; in contrast, the lower turn-on electric field and emission current of CNCs made them more durable under such a high working voltage. However, the emission current of the CNCs is a bit too low to achieve a good lighting efficiency in FELs. Therefore, it is important to enhance the current density of CNC cathodes to meet the requirement (2–5 mA at 8 kV in our case) on FEL operation.

In the literature, it is well-known that the FE characteristics of CNTs can be enhanced by nitrogen-doping [28–30]. The periodic distribution of pentagonal and heptagonal carbon rings in CNCs indicates that CNCs can be hydrogenated and nitrogen-doped more easily [31,32]. In this study, we propose a simple method to reduce the voltage of the turn-on electric field of CNC cathodes and substantially enhance the FE characteristics of FELs by post-treating the CNCs with nitrogen.

## 2. Experimental

### 2.1. Synthesis of Pd catalyst and substrate pretreatment

In this study, a poly(styrene-co-NIPAAm)/Pd catalyst was prepared and used to synthesize CNCs for use as FE cathodes. We had previously developed a temperature-responsive Pd catalyst (poly(styrene-co-NIPAAm)/Pd nanoparticles) for use in electroless nickel deposition [33] and CNT/CNC synthesis. The substrates used for the synthesis of CNC cathodes were 304 stainless steel wires with a length of 5.5 cm and a diameter of 1 mm. The substrate was first cleaned with acetone and ultrasonicated for 30 min. The substrate surface was then roughened by sandblasting with 220-grit sand.

### 2.2. Synthesis of carbon nanocoils by thermal chemical vapor deposition

Before thermal chemical vapor deposition (TCVD), the Pd catalyst was deposited on the wire substrates by dipping the wires into a poly(styrene-co-NIPAAm)/Pd solution and then drying them at 80 °C in air. Fig. 1 shows a schematic of TCVD. The wires were placed at the center of a quartz tube, which was heated by a furnace and equipped with a gas-flow controlling system. Subsequently, 5 sccm acetylene, 100 sccm argon, and 20 sccm hydrogen were introduced into the furnace; these gases were used as the carbon source, carrier gas, and reductive gas, respectively.

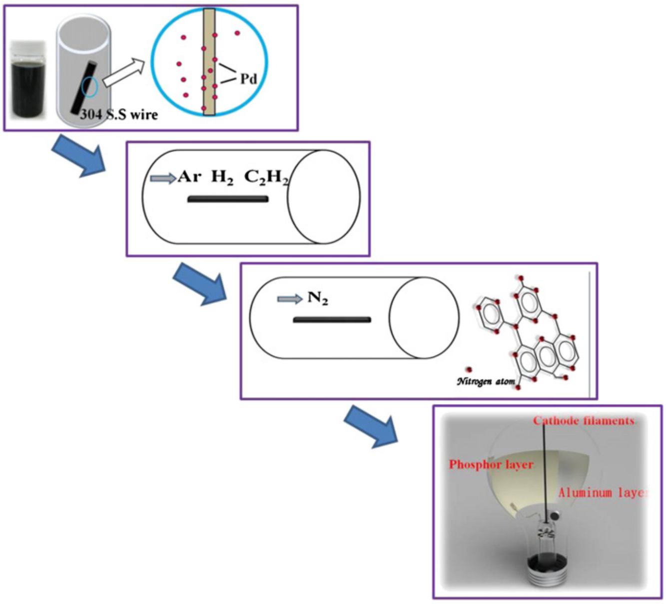

**Fig. 1.** Schematic depicting the proposed experimental process for FEL cathode preparation and device fabrication: dip coating of Pd catalysts; TCVD growth of CNCs; nitrogen post-treatment; and the assembly of a bulb FEL.

A heating ramp was used for 25–40 min to reach the desired process temperature (500–800 °C), and acetylene was introduced into the reaction tube for 30 min. After cooling the reaction system to room temperature, CNC cathode filaments (hereafter also referred to as "samples") were obtained. The morphologies of the samples were examined using a transmission electron microscope (TEM) (model FEI Tecnai F30) and a field-emission scanning electron microscope (FE-SEM) (model: JEOL JSM-7600F).

### 2.3. Nitrogen post-treatment

The as-grown CNC cathode filaments were doped with nitrogen at various temperatures (200, 300, and 400 °C) using various nitrogen flow rates (15, 80, 500, and 2600 sccm) for 30 min. The morphologies of the CNC filaments before and after nitrogen treatment were observed using the FE-SEM. The crystallinity of and defects in the nitrogen-doped CNCs were analyzed using Raman spectroscopy (model: Renishaw inVia). The degree of nitrogen doping was analyzed using electron spectroscopy for chemical analysis (ESCA) (model: ULVAC-PHI 1600).

### 2.4. Field emission tests

Bulb-type and planar-type geometries were used for the FE tests. The bulb-type FE device is shown in Fig. 1. This device consisted of a glass bulb (diameter: 6 cm), the inner surface of which was covered with an aluminum film. A phosphor layer on the aluminum film acted as the anode. A nitrogen-treated CNC cathode filament was combined with the bulb anode in a $3 \times 10^{-6}$ Torr vacuum to form an FEL. The FEL bulb was tested in a vacuum chamber at high voltages (0–10 kV). However, the *E*-field distribution for this geometry could not be determined analytically, and according to our research, no related numerical simulation has been reported. Therefore, we considered the traditional planar test geometry (in which $E = V/d$) for the measurement of the turn-on electric field of the CNCs as the second method for evaluating the results obtained for the bulb device and determining the value of the turn-on electric field. Additionally, we aged the cathode wires before the test by turning them on to a high voltage and off repeatedly more than 50 times until the emitters were very stable.

In the planar test geometry, the planar substrates used for the synthesis of CNC cathodes were ITO glass. The substrate was first cleaned with acetone and then ultrasonicated for 30 min. The Pd catalyst was deposited on the planar substrates by dipping with the poly(styrene-co-NIPAAm)/Pd solution and then drying at 80 °C in air.

Then, CNCs were synthesized using CVD on the surface of an ITO-coated glass plate as the cathode. The as-deposited or nitrogen-doped CNC film on the ITO glass was used as the FE cathode and another ITO-coated glass substrate was used as the anode. The flat electrodes were $1 \times 1$ cm$^2$ in size and the gap between the parallel electrodes was set at 400 μm. The FE J–E curves of these assembled FE elements were tested at voltages of 0–1 kV.

## 3. Results and discussion

### 3.1. Carbon nanocoil growth on 304 stainless steel wires with Pd catalyst nanoparticles

In our previous studies [33], we developed a new temperature-responsive Pd catalyst (poly(styrene-co-NIPAAm)/Pd nanoparticles). As shown in Ref. [33], poly-N-isopropylacrylamide (PNIPAAm) is a temperature-sensitive polymer which can stably and uniformly disperse the nano-Pd catalyst particles in aqueous solution below 305 K. The Pd nanoparticles exhibited satisfactory dispersion in water devoid of any