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Improve photocurrent quantum efficiency of carbon nanotube by chemical treatment

Hongguang Wang, Jinquan Wei*, Yi Jia, Zhen Li, Hongwei Zhu, Kunlin Wang, Dehai Wu

Key Lab for Advanced Materials Processing Technology of Education Ministry, Department of Mechanical Engineering, Tsinghua University, Beijing 100084, China

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ABSTRACT

High photocurrent quantum efficiency (QE) of carbon nanotubes (CNTs) is important to their photovoltaic applications. The ability of photocurrent generation of CNTs depends on their band structure and surface state. For given CNTs, it is possible to improve the QE of photocurrent by chemical modification. Here, we study the effects of simple chemical treatment on the QE of CNTs by measuring the photocurrent of macroscopic CNT bundles. The QE of the H_2O_2-treated CNT bundle reaches 5.28% at 0.1 V bias voltage at a laser (λ = 473 nm) illumination, which is 85% higher than that of the pristine sample. But the QE of the CNTs treated in concentrated HNO_3 is lower than that of the pristine sample. It shows that moderate chemical treatment can enhance the photocurrent QE and excessive chemical treatment will decrease the QE because of introducing lots of structural defects.

1. Introduction

Due to unique electrical and optoelectronic properties, carbon nanotubes (CNTs) have great potential applications in light sensor and photovoltaic devices [1–11]. It has been reported that CNTs can enhance the performance of the solar cells. The performance of solar cells are improved significantly, when small amount (~1 wt%) CNTs were added into active layer of organic solar cells [4–8]. The improvement in performance of the organic solar cells by adding CNTs derives not only from collecting charges and offering percolation path for charges, but also from generating photo-induced carriers [6–10]. Thus, one possible way to improve the efficiency of solar cells is to enhance the photo-induced carrier generation ability of CNTs.

When illuminated by light, CNTs might generate elastic response, photocurrent and photoconductivity [12–16]. Recently, the photocurrent and/or photoconductivity of the CNTs have been studied widely. It has been reported that the energy conversion rate of the photoconductivity was about 10% for the CNT field effect transistor [13], and 10–20% for the CNT p–n junction [15]. The photocurrent and photoconductivity were enhanced significantly when the light irradiates on the p–n junction, homo- or hetero-junction between CNTs and other materials [17–21]. The photocurrent derives from the interaction between incident photon and electrons in CNTs, which is affected by the band structure of CNTs [22]. Because photo-induced carriers can transfer from the attached functional groups to CNTs, the optoelectronic ability of the CNTs is improved significantly when they are modified by photosensitive dyes [23,24]. How to improve the photocurrent quantum efficiency (QE) of the CNTs to make them widely use in photovoltaic devices? Here, we try to improve the QE of CNTs by tailoring their surface state through simple chemical treatment.

2. Experimental

2.1. Sample preparation

The macroscopic CNTs used in our experiments are prepared by floating chemical vapor deposition (CVD) method, using xylene as carbon feedstock and ferrocene as catalyst precursor, which was described in details recently [25]. The as-grown CNT samples usually contain some impurities, such as amorphous carbon and catalyst particles. To remove the impurities, the as-grown CNTs are soaked in 30 wt% H_2O_2 and concentrated HCl (37 wt%) solution for 24 h at room temperature and then rinsed with distilled water to pH = 7 (denote as H_2O_2-treated CNTs). A portion of H_2O_2-treated samples are further soaked in concentrated HNO_3 (70 wt%) solution for 24 h and then rinsed in distilled water to pH = 7 (denote as HNO_3-treated CNTs) to dope the CNTs by hole injection [26]. The CNTs are still in macroscopic film even after treating in HNO_3 solution. Some centimeter-long bundles are drawn from the CNT film in water solution for photocurrent testing.

2.2. Photocurrent measurement

The photocurrent measurement is similar to that we did recently [1,18], where a long CNT bundle is suspended between two copper electrodes with a distance of 10 mm. Typically, a uniform CNT

* Corresponding author. Tel.: +86 10 62781065; fax: +86 10 62770190.
E-mail address: jqwei@tsinghua.edu.cn (J. Wei).

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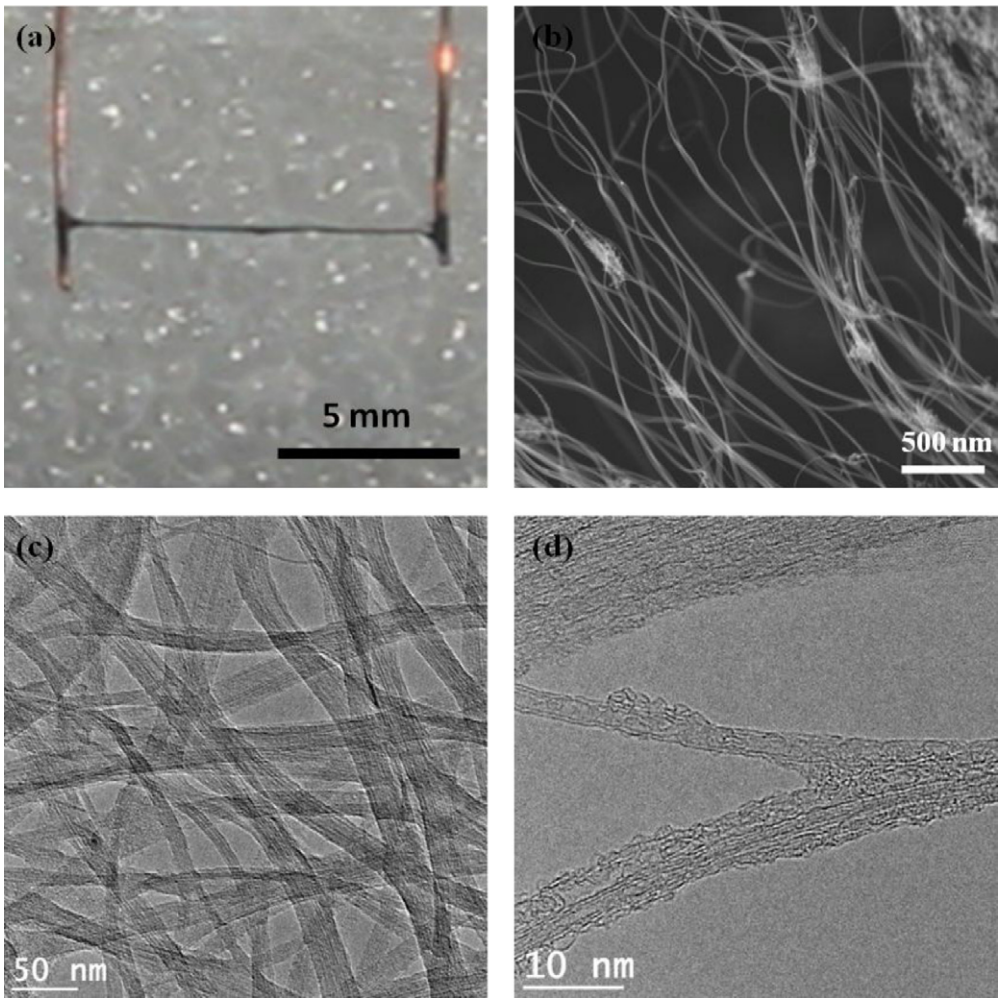

Fig. 1. (a) Optical images of CNT bundle for photocurrent testing. (b) SEM image of the as-grown CNT film. (c) TEM image of the H_2O_2-treated CNTs. (d) HRTEM image of the H_2O_2-treated CNTs.

bundle drawn from the CNT film in water solution is connected with two copper electrodes (Fig. 1a). When the water dries up, the CNT bundle shrinks and grasps electrodes tightly. The diameter of the CNT bundles for photocurrent measurement is measured by SEM, which are 150 μm, 60 μm, 80 μm for the as-grown, H_2O_2-treated and HNO_3-treated samples, respectively. The *I–V* curves of the CNT bundles with and without light illumination are measured by a Keithley sourcemeter.

2.3. Characterization

The CNT bundles (as-grown, H_2O_2-treated and HNO_3-treated) were characterized using scanning electron microscope (SEM, FEI Quanta 400), transmission electron microscope (TEM, JEOL-2100F), Raman spectroscopy (Renishaw RM-2000), Fourier transform infrared spectrum (FTIR, Nicolet-5700) and ultraviolet–visible (UV) spectrum (UV, Hitachi U-3010). Raman spectra are carried out on the suspending CNT bundles at a laser ($\lambda = 632.8$ nm) excitation after the photocurrent measurement. The CNT films for FTIR and UV spectra measurement are prepared from water by drying at 80 °C in a vacuum oven overnight.

3. Results and discussion

Fig. 1b shows a SEM image of the as-grown CNT films, showing that the films consist of very long CNTs. Some catalyst particles are also identified in the samples. Fig. 1c is a TEM image of the H_2O_2-treated CNT samples. It is clear to show that the CNTs assemble in bundles. The CNT films are very clean and most of the catalyst particles are removed from the CNT samples after H_2O_2 treatment. Fig. 1d demonstrates a high resolution TEM image of the H_2O_2 treated samples, showing that the CNT films consist mainly of single- and double-walled CNTs with diameters of 1–3 nm.

Fig. 2 shows SEM images of the three CNT bundles. The CNTs are aligned in the axial direction of the bundles. The CNT bundles have uniform in diameter along the axis direction. Some catalyst particles encapsulated in amorphous carbon are observed in the as-grown bundles (Fig. 2a). But most of the catalyst particles are removed from the samples after H_2O_2 treatment. Thus, both of the H_2O_2-treated and HNO_3-treated CNT bundles are cleaner denser than the as-grown bundle, which decrease the contact resistance between CNTs (Fig. 2b and c). It is hard to distinguish the H_2O_2-treated CNT sample from the HNO_3-treated CNT sample under SEM.

At illumination, the current pass through the CNT bundles can be expressed as $I = I_{dark} + I_{ph}$, where I_{dark} is the current in dark and I_{ph} is the photo-induced current (photocurrent). The I_{ph} of the CNT bundle depends on diameter of bundle, bias voltage, power intensity and photon energy of incident light. For a given bias voltage, the I_{ph} is linear to the intensity of incident light [1]. Fig. 3a shows the I_{ph}–V_{bias} curves of the as-grown CNT bundle illuminated by three types of laser with wavelength of 473 nm (spot size: 2.5 mm, power density: 20.4 mW mm^{-2}), 532 nm (spot