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Photoconductivity enhancement in alkali metal doped multiwall carbon nanotubes

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ABSTRACT

Photoconductivity effects in pristine and alkali-metal (K, Li) doped multiwalled carbon nanotubes (CNTs) were studied under xenon (100 mW) and also halogen (10 mW) light continues sources. To perform the measurements, the pristine and alkali doped CNTs were deposited into pores of a silver foam plate with nano-metric porosity by electrophoresis technique. The foam acted as a conducting frame for sweeping the photo-induced electrons to prevent rapid local electron–hole recombination in the CNTs. The radiation spectrum of the xenon source was similar to the Sun light spectrum and under normal ambient condition the photocurrents in the alkali doped samples were enhanced noticeably in comparison with the pristine CNTs. These results present a functional photoconductive performance of a heap of as-prepared alkali-metal doped CNTs that would be applicable as a light sensor without the necessity of separation between metallic and semiconducting CNTs (m- and s-CNTs).

1. Introduction

Nowadays too many optical studies have been conducted on optical and photoconductive properties of the CNTs [1–7]. The main applications of the photoconductivity effect are in the solar cell and photo-detector technologies [8]. Obviously, for all the applications the semiconducting properties of the CNTs are essential. So far, the prominent ways to growth the CNTs are chemical vapor deposition (CVD) or arc-discharge methods and unfortunately in both of them there is no certain control on the growth procedure; therefore, the metallic and semiconducting types of CNTs are produced altogether.

In this regard, the photoconductivity effect presents an efficient functional application for the semiconducting CNTs (s-CNTs) without the necessity of physical separation from the metallic tubes, which is a complex and expensive procedure.

Levitsky et al. (2003) [9] have studied the photoconductivity of a thin film of single walled CNTs under continuous-wave illumination and the photocurrent exhibits a linear response with bias voltage up to 5 V. Shaoxin et al. (2006) [10] have mounted a similar single walled CNT film between two platinum electrodes under pulsed laser and vacuum condition to find out a position dependent photoconductivity effect of the metal-CNTs junctions because of a strong charge separation at their interfaces. In this regard, Salvato et al. (2008) [11] have used single walled CNTs bundles whose axes are aligned along the direction of the externally supplied bias current and experimentally found that a charge transport model governed by the tunneling through the metal-CNTs junction potential barriers.

Furthermore, Costia et al. (2009) [12] found that the photoconductivity in multi-walled CNTs under white light illumination is a linear function of either the bias voltage or the optical power density in the wide range from IR to UV. On the other hand, many studies (for instance [13]) have shown that all the electrical and magnetic characteristics of the CNTs are changeable via doping procedure and theoretically it would be possible by doping alkali metals in the s-CNTs their semiconducting and also their photoconducting properties to be regulated for empirical applications (because doping of the alkali metals increase electron density in the conduction band of the doped CNTs).

Salvato et al. (2011) [14] have investigated the effect of potassium doping on the transport properties of aligned single-walled CNT fibers. They found that the I–V (current-voltage) characteristics and the magnetoresistance of the fibers consistently show that doping enhances the metallic character of the fibers and at higher than a characteristic temperature; enhancement in the K-doped sample is due to the increase of the density of states, which raises carrier's hopping.

In this report we have studied the photoconductivity effect via conductivity enhancement of a silver foam plate (with nanometric

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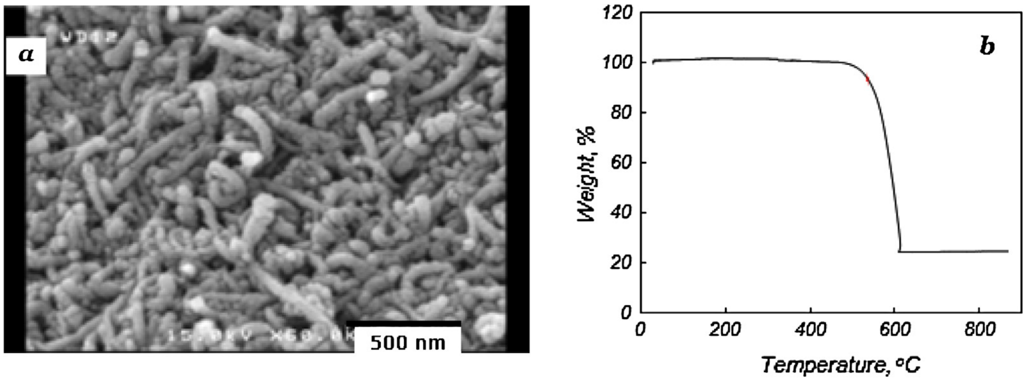

Fig. 1. (a) SEM image of the as prepared multi walled CNTs (some of the catalyst particles at the end of the tubes can be seen), (b) TGA graph for the as prepared nanotubes and it is seen that the majority of the graphitized sample have burned around 550 °C.

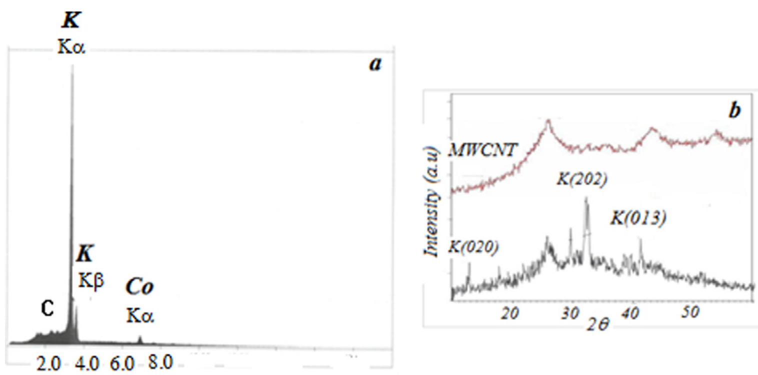

Fig. 2. (a) EDAX analysis of the potassium doped CNTs (resolution for light elements like carbon is not high sufficiently and also a trace of the Co catalyst can be spotted), (b) XRD comparison between the K-doped and pristine CNTs (Miller indices for some of the potassium's reflections have been shown, as well).

porosity) loaded by multi-walled CNTs under continues illumination of xenon or halogen light sources in the normal air pressure. The purified pristine CNTs and alkali metal (K, Li) doped samples were loaded and deposited to the pores of the foam by electrophoresis deposition method (EPD). The alkali impurities act as donor centers for the s-CNTs and could impact on the photoconductivity of the doped CNTs substantially.

2. Sample preparation and the experimental set up

2.1. Sample preparation

The used multi walled CNTs in this study have been synthesized by the CVD method (with cobalt particles catalyst) and they were purified by acidic and thermal treatments [15,16]. The purity level of the sample has been confirmed by X-ray diffraction (XRD), transmitted electron microscope (TEM) and thermal gravimetric analysis (TGA) techniques, as shown in Fig. 1. In this regard, the sharp slope of the TGA curve indicates that the CNTs burning temperature is around 550 °C.

In order to dope the alkali metals into the CNTs we have followed Chun et al. (2006) [17] recipe: "adding 50 mg of the CNTs to 0.2 molar solution of Phenantheren and Etilengelicol DM plus 100 mg of K or Li". By using energy dispersive X-ray analysis (EDAX) and XRD techniques the doping of potassium in the CNTs was confirmed (the presence of residual cobalt catalyst particles can be traced) as shown in Fig. 2.

Next, the pristine and alkali-doped and CNT particles were loaded on surface and also inside the pores of some silver foam plates through the EPD method. The foam plates (dimensions: 2 × 1 cm) with nanoscale porosity acted as a solid conducting net holder for the deposited pristine and doped CNT particles; therefore, the prepared Ag-CNTs sample plates included lots of microscopic inter-junctions between the foam pores and the CNT particles, as shown in Fig. 3. These sample plates not only showed reasonable physical stability (without using any glue or additional binders for holding the CNTs) but also were able to facilitate charge transferring procedure from the s-CNTs to the silver network so the electron–hole recombination process, which is a negative factor in the photoconductivity measurements, could be blocked.

To perform the EPD procedure, an electrochemical cell was used that consisted of the Ag foam plate and a Pt plate as the electrodes and a dilute suspension of the doped-CNTs in ethanol as the electrolyte. The biased potential was 80 V for about 15 minutes [18], and also to avoid agglomeration of the CNTs in the suspension, the whole cell was placed inside a low frequency vibrating bath.

2.2. Photoconductive measurement set up

The measurements have been performed by employing a "solar simulator unit" that was comprised of: (a) A continues xenon light source with similar Sun light's spectra (wavelength range: 280–800 nm); (b) A sealed cavity with light homogenizer plates; (c) High regulated power supply and digital I/V micrometer.

The sample plates were mounted in the cavity and the I–V measurements have been collected under dark and light conditions. On the other hand, to avoid the effect of the UV radiation part of the xenon source, we also have used a white halogen light source for the complimentary measurements.

3. Results and discussions

3.1. Photoconductivity in silver foam deposited by pristine CNTs

Fig. 4 shows the I–V characteristic curves for the pristine CNTs loaded foam plate under dark and xenon light exposure. In the