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Synthesis of silver nanoparticles on surface-functionalized multi-walled carbon nanotubes by ultraviolet initiated photo-reduction method

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ABSTRACT

In this article, we described a new, facile method on fabrication of multi-walled carbon nanotubes (MWNTs) with silver nanoparticles by an ultraviolet initiated method. MWNTs were functionalized with acrylic acid to introduce carboxylic acid groups, and then the Ag nanoparticles were synthesized on the functionalized MWNTs by using of ultraviolet irradiation without adding of any protective or reductive agent. The obtained MWNTs/Ag composites were analyzed with Fourier transform infrared spectrometer (FT-IR) spectroscopy, transmission electron microscope (TEM), X-ray powder diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). It was confirmed that Ag nanoparticles with diameters in a region of 5–10 nm were anchored on the surface of MWNTs by an interaction of Ag and oxygen in the carboxyl group.

1. Introduction

Since their discovery in 1991 [1], carbon nanotubes (CNTs) have attracted much attention because of their mechanical properties, thermal and chemical stability, and good electronic properties [2]. Due to their nanoscale dimensions and high surface area, CNTs are also considered as efficient templates for assembling metallic nanoparticles, which allow their fictionalization with a variety of nanostructures in two or three dimensions [3]. CNTs decorated with metal nanocrystals were widely used in biosensor [4], catalysts [5] and antimicrobial agent [6]. In this area, as a new class of the multifunctional materials, composites of carbon nanotube-silver nanoparticles (CNT/Ag) have been extensively investigated in the past decade. A few interesting routes have been proposed to attach certain Ag nanoparticles onto CNTs, including radiation-induced reduction of silver ions [7], chemical in situ reduction method [8], electrochemical deposition [9] and electroless deposition with or without the aid of reducing agents etc. [10,11]. However, due to the complicated fabrication process and expensive equipment costs, thus, simple and effective ways to decorate CNTs with silver particle are still being pursued.

To control the nucleation and growth of Ag nanoparticles on CNTs, it will be important to control surface functionality of CNTs and the additives during Ag deposition. Among the different functional groups, carboxylic group was widely used as a nucleation site for the deposition of metal clusters [12,13]. The carboxylic group can be introduced to CNTs surface through various oxidation methods [14,15]. However, the functionalization of CNTs with oxidation methods was usually at the cost of their physical properties. Therefore, it will be desired to develop a non-oxidative approach that functionalizes uniformly carboxylic groups on CNTs with high density.

In this paper, we adopted a non-oxidative approach to functionalize MWNTs with PAA for subsequent decoration of Ag nanoparticles. Compared to the previous methods, a convenient approach for decorating MWNTs with Ag nanoparticles was proposed by ultraviolet irradiation photo-reduction without any protective or reductive agents. Different methods were utilized to characterize the formation and structure of the formed composites.

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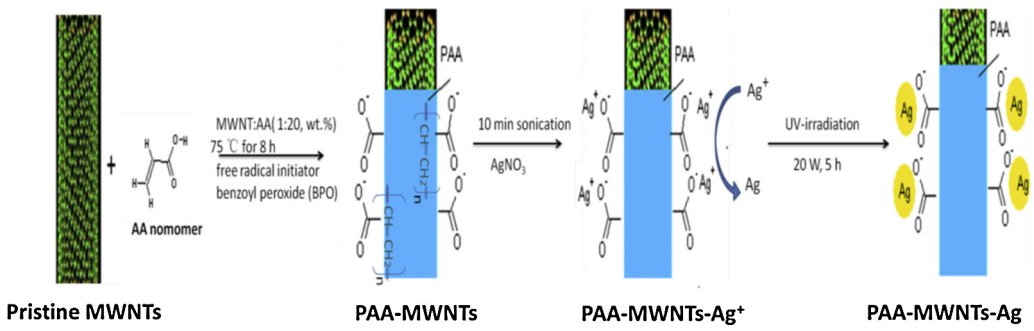

Scheme 1. The schematic diagram of the decoration MWNTs with PAA and Ag nanoparticles.

2. Experimental

2.1. General procedures

A non-oxidative approach was adopted to functionalize MWNTs by use of poly(acrylic acid) (PAA) with high density and uniformity. The Ag particles were anchored onto the MWNTs during their synthesis by irradiating the mixture of the PAA-functionalized MWNTs and silver nitrate with two ultraviolet lamps (Scheme 1).

2.2. Materials

MWNTs (purity > 95 wt.%, 40–60 nm diameter, 5–15 μm length) were synthesized by the chemical vapor deposition and purchased from Shenzhen Nanotech Port Co. Ltd (ShenZhen, China). Acrylic acid, benzoyl peroxide and silver nitrate were all purchased from Sigma–Aldrich. All other reagents, such as acetone, toluene, and ethanol were analytical grade. The water used in this paper was prepared using double distilled and subsequently deionised Millipore water.

2.3. Functionalization of MWNTs with PAA (PAA-MWNTs)

The Functionalization of MWNTs with PAA was referred to the previous report [16]. In a typical experiment, a certain quality of acrylic acid and 0.1 g MWNTs (with mass ratio of 50/1, 20/1 and 10/1) were mixed with 100 ml acetone in a three-neck round bottom flask. After 10 min ultrasonic dispersion (SK3300HP), the oxygen was removed by bubbling of nitrogen for 30 min, and then 0.05 g free radical initiator benzoyl peroxide was added into the mixture. The reaction was kept at 75 °C for different time from 0.5 h to 8 h to vary the amount of PAA on MWNTs. The polymer-modified MWNTs were carefully filtered to remove the excess PAA, and then dried at 80 °C for 14 h. The obtained PAA-modified MWNTs powders were analyzed with FT-IR (AVATAR360, 4000–400 cm^{-1}, Nicolet, USA). Thermo gravimetric analyses (TGA) of the PAA-modified MWNTs were performed on an instrument of HCT-1 TGA with a platinum pan. The powers were heated from 50 °C to 800 °C at a heating rate of 10 °C/min under nitrogen (flow rate 20 mL/min).

2.4. Decoration of the PAA-MWNTs with Ag particles (PAA-MWNTs/Ag)

In a beaker, 50 mg PAA-MWNTs powders formed above were added into 10 ml $AgNO_3$ solution (5 mM). The mixed solution was dispersed in an ultrasonic bath for 10 min, and then irradiated by ultraviolet light with two 20 W low-pressure mercury lamps at room temperature for 5 h. After irradiation, the PAA-MWNTs/Ag composites were carefully filtered with plenty of water, and dried at 80 °C for 2 h. TEM micrographs of the obtained hybrid composites were observed using a Hitachi Model H-700 transmission electron microscope, with an accelerating voltage of 200 kV. Elemental

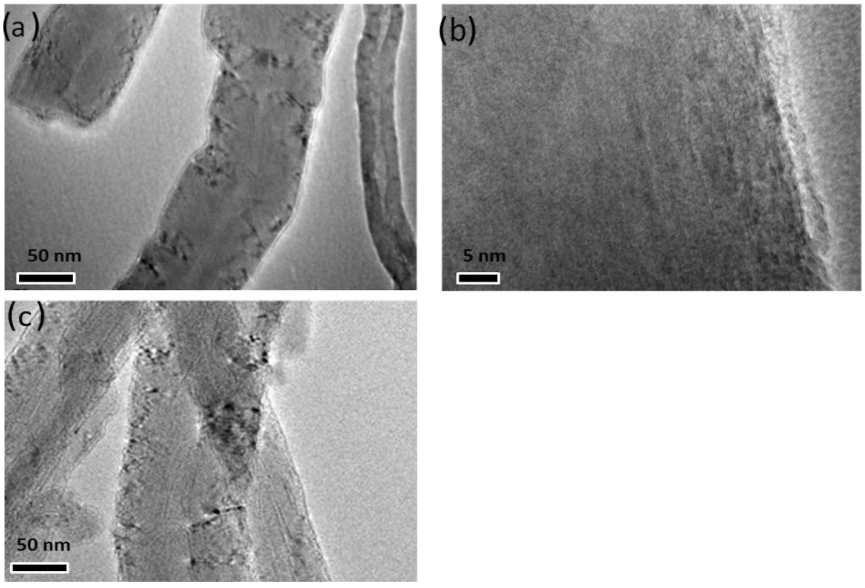

Fig. 1. (a, b) TEM images of PAA-MWNTs, (c) TEM image of the pristine MWNTs. The PAA-MWNTs was formed at 75 °C for 5 h reaction with a AA/MWNTs weight ratio of 20:1.