

# Synthesis of magnetic carbon nanotubes: Functionalisation of carbon nanotubes with nickel/sulphur nanoparticles via self-assembly in near-critical acetone



Yoshihiro Katsube<sup>a</sup>, Takahiro Fukuda<sup>b</sup>, Toru Maekawa<sup>a,b,\*</sup>

<sup>a</sup> Graduate School of Interdisciplinary New Science, Toyo University, 2100 Kujirai, Kawagoe, Saitama 350-8585, Japan

<sup>b</sup> Bio-Nano Electronics Research Centre, Toyo University, 2100 Kujirai, Kawagoe, Saitama 350-8585, Japan

## ARTICLE INFO

### Article history:

Received 1 May 2013

Received in revised form 6 August 2013

Accepted 15 August 2013

### Keywords:

Carbon nanotubes

Nanoparticles

Nickelocene

Sulphur

Acetone

Magnetisation

Near-critical fluid

## ABSTRACT

Magnetic carbon nanotubes (CNTs); i.e., magnetic materials-filling or -coating CNTs, have recently been paid a lot of attention to particularly in the bio-medical field aiming to develop high resolution nano bio-imaging media, nano hyperthermia materials, nano drug delivery vehicles and nano-surgical robots. Fluids under their near-critical conditions, which are called near-critical fluids, are often used in chemical science and engineering; e.g., for the extraction of chemicals, and can also be utilised for an efficient synthesis of nanomaterials. Here, we functionalise CNTs with carbon-coating nickel/sulphur nanoparticles via self-assembly by mixing CNTs, nickelocene and sulphur with acetone and setting the solvent under sub-critical or super-critical conditions. We find that each nanoparticle is composed of a mixture of NiS and Ni<sub>3</sub>S<sub>2</sub> covered with a carbon shell and that the size of the nanoparticle changes depending on the fluid temperature; i.e., the average diameter of the core nanoparticle increases with an increase in the synthetic temperature. Each CNT is also covered with a carbon layer. The CNTs immobilised with the carbon-coating nanoparticles show soft ferromagnetic characteristics. The magnetisation is also increased with an increase in the synthetic temperature. The present methodology may well be applied to the synthesis of other magnetic carbon nanomaterials such as magnetic fullerenes and graphenes, by dispersing fullerenes and graphenes in near-critical fluids, in which metalloenes and sulphur are dissolved.

© 2013 Elsevier B.V. All rights reserved.

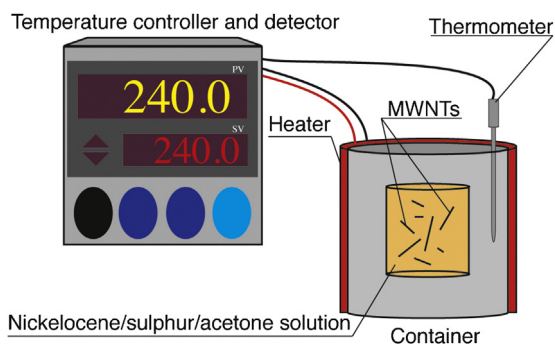
## 1. Introduction

Carbon nanotubes (CNTs) were discovered among the deposits on a cathode after a carbon arc-discharge experiment [1]. Since then, several synthetic methodologies of CNTs have been invented. The chemical vapour deposition (CVD) and laser vapourisation methods are commonly employed nowadays [2,3]. CNTs have been used as nanoprobe for scanning probe microscopes, field emission displays and field effect transistors [4–6]. Multi-walled CNTs (MWNTs) and carbon onions are composed of multi layers of graphitic cylinders and spheres. Various materials such as fullerenes, metals and aqueous liquid have been successfully captured by CNTs and carbon onions [7–12], whereas DNA, reversible cyclic peptides and metal particles have been immobilised on the surface of CNTs [13–16]. Metal-filling and -coating carbon nanostructures are expected to be used for drug delivery

vehicles, protectors of nanomaterials from oxidation, hydrogen storage and high-density magnetic recording media [17–20]. Magnetic CNTs and magnetic carbon onions; i.e., magnetic materials-filling or -coating CNTs and carbon onions, are important nanomaterials particularly in the bio-medical field for the development of high resolution bio-imaging media, nano hyperthermia materials, nano drug delivery vehicles and nano-surgical robots [9,16,17,21–23]. There are two ways for functionalising CNTs with foreign materials; i.e., (a) Materials are intercalated into or attached to CNTs during the growth process of CNTs; and (b) Materials are inserted into or attached to pre-made CNTs. Metals such as chrome, iron and nickel were intercalated into CNTs during the growth process of CNTs by arc-discharge and CVD [24–27], noting that the above metals were in fact used as catalysts, whereas some advance process such as oxidation, chemical modification or purification are necessary for the production of materials-filling or -coating CNTs via the insertion of materials into or attachment of materials to pre-made CNTs [28–30], noting that the original shape of the CNTs maintains in this case. Although several innovative methodologies have been invented for the creation of magnetic CNTs [9,16], some simpler ones for producing a large quantity of magnetic materials-filling or -coating CNTs are still demanded.

\* Corresponding author at: Bio-Nano Electronics Research Centre, Toyo University, 2100 Kujirai, Kawagoe, Saitama 350-8585, Japan. Tel.: +81 49 239 1375; fax: +81 49 234 2502.

E-mail address: [maekawa@toyo.jp](mailto:maekawa@toyo.jp) (T. Maekawa).



**Fig. 1.** Outline of the experimental system. The solution of MWNTs, nickelocene and sulphur dissolved in acetone was introduced into a cylindrical container made of stainless steel. The temperature of the fluid was controlled by a heater installed around the container and a temperature regulator. The density of acetone in the container was set at the critical value. The state of the fluid was changed from a sub-critical gas–liquid two-phase region at 25 °C to 100, 150, 200, 240, 260 and 280 °C along the gas–liquid coexistence curve. Each experiment was carried out for 1 h at the prescribed temperature.

Super-critical fluids, the pressure and temperature of which are higher than those at the critical points, have gas-like diffusivity and liquid-like solubility. The solubilities of chemicals in near-critical fluids greatly change depending on the pressure and temperature and therefore near-critical fluids are often used for the extraction of chemicals [31–34] and for the cleaning and washing of semiconductors [35,36].

In this paper, we produce magnetic CNTs, dispersing pre-made CNTs in acetone, in which nickelocene;  $\text{Ni}(\text{cp})_2$ , and sulphur are dissolved, and setting the solvent under sub-critical or super-critical conditions. We find that carbon-coating nickel/sulphur nanoparticles are self-assembled and attached to CNTs. The effect of the synthetic temperature on the size and magnetisation of the particles is clarified. The present methodology may well be applied to the synthesis of other magnetic carbon nanomaterials such as magnetic fullerenes and graphenes.

## 2. Materials and methods

An outline of the experimental system is shown in Fig. 1. MWNTs were produced in advance by arc discharge without using any catalysts. The average internal diameter, the length and the number of walls of the MWNTs were, respectively, 3.1 nm, 350.0 nm and 15. MWNTs, nickelocene and sulphur were dissolved in acetone, where the mass concentration of MWNTs was set at  $1.0 \text{ mg ml}^{-1}$  and the molar concentrations of nickelocene and sulphur were, respectively,  $2.5 \times 10^{-9}$  and  $5.0 \times 10^{-9} \text{ mol l}^{-1}$ . Since nickelocene is highly sensitive to oxygen [37], we stored nickelocene with an oxygen absorber (A-500HS, I.S.O. Inc.), which was composed of iron powders and clay minerals, in a closed vacuum container under refrigeration. Before each experiment, we dissolved nickelocene, sulphur and MWNTs in acetone within 3 min after nickelocene had been taken out from the container. The solution of the MWNTs, nickelocene and sulphur dissolved in acetone was introduced into a cylindrical container made of stainless steel. The inner and outer diameters and inner and outer heights of the container were, respectively, 13.0 and 59.6 mm, and 26.6 and 56.1 mm. A platinum resistance thermometer (Pt100, Chino Co. Ltd.) was set in the container wall and the temperature of the fluid was controlled by a heater installed around the container and a temperature regulator (LT470, Chino Co. Ltd.). The density of acetone in the container was set at the critical value [38], injecting the solution composed of 1.2 ml of acetone, nickelocene, sulphur and MWNTs into the closed test container, the volume of which was 3.5 ml. The state of the fluid was changed from a sub-critical gas–liquid

two-phase region at 25 °C to 100, 150, 200, 240, 260 and 280 °C along the gas–liquid coexistence curve by raising the fluid temperature at an increase rate of  $18.0 \text{ °C min}^{-1}$ . We confirmed that critical opalescence occurred at the critical temperature. Note that the critical temperature  $T_c$ , pressure  $P_c$ , and density  $\rho_c$  of acetone are  $T_c = 235.5 \text{ °C}$ ,  $P_c = 4.76 \text{ MPa}$  and  $\rho_c = 273 \text{ kg m}^{-3}$  [38]. Each experiment was carried out at least five times for 1 h at the prescribed temperature; i.e., 25, 100, 150, 200, 240, 260 or 280 °C. After experiment, the temperature was decreased gradually down to 25 °C. We centrifuged the solution and the supernatant was discarded. The residuals were collected and dried in a vacuum chamber and then we analysed the structures of the residuals by transmission electron microscopes (TEMs) (JEM2200FS, JEOL and JEM2100, JEOL) and the selected area electron diffraction (SAED) method (JEM2200FS, JEOL) without any coating on the surface of them. The elementary components of the structures were analysed by energy-disperse X-ray spectroscopy (EDS) (JED2300T, JOEL). The magnetic properties were measured by a vibrating sample magnetometer (VSM) (7407, Lake Shore Crytronics Inc.).

## 3. Results and discussion

The solution of MWNTs, nickelocene and sulphur dissolved in acetone was left in the container for 1 h, keeping the temperature at 25, 100, 150, 200, 240, 260 or 280 °C as mentioned. Note that the pressure corresponding to the temperature; 100, 150, 200, 240, 260 and 280 °C, is 0.37, 1.16, 2.80, 6.96, 8.60 and 10.24 MPa according to the Antoine and van der Waals equations [39,40]. Fig. 2 shows TEM images of MWNT/nanoparticles hybrid structures obtained after the experiment. MWNTs were successfully modified with nanoparticles when the temperature was 200 and 240 °C, whereas there was no modification with any particles or layers on the surface of MWNTs at 25 °C and MWNTs were covered with some layers at 100 °C. The number of nanoparticles attached to the surface of MWNTs was much smaller at 150 °C than that at 200 and 240 °C (see the Supplementary Data for TEM images of MWNTs synthesised at 100 and 150 °C). TEM image, SAED pattern and EDS mappings of an MWNT modified with nanoparticles, which were synthesised at 240 °C, are shown in Fig. 3. According to the EDS analysis (see Fig. 3(c)–(e)), particles, which were composed of nickel and sulphur covered with carbon shells, were attached to the surface of the MWNT. The surface of the MWNTs was also covered with carbon layers. The SAED pattern shows that nanoparticles, which were made up of a mixture of rhombohedral nickel sulphide;  $\text{NiS}$  [41], and trinickel disulphide;  $\text{Ni}_3\text{S}_2$  [42], were covered with a layer of amorphous carbon (see Fig. 3(b)). It is supposed that those nanoparticles were attached to the surface of MWNTs thanks to the amorphous carbon layers covering both nanoparticles and MWNTs. The diameters of nanoparticles were measured from TEM images, targeting 100 particles. The diameter of the core of the nanoparticle created at 150, 200 and 240 °C was, respectively,  $4.9 \pm 2.0$ ,  $6.6 \pm 2.0$  and  $10.3 \pm 2.8 \text{ nm}$  (see the Supplementary Data for the distributions of the diameters of the nanoparticles). The thickness of the carbon layers at 150, 200 and 240 °C was more or less the same; i.e., 4.0, 4.0 and 4.3 nm, respectively, at 150, 200 and 240 °C. It is important to note that no nanoparticles were formed without mixing sulphur with the solution, in which case MWNTs were covered with amorphous layers composed of nickel and carbon (see the Supplementary Data for a TEM image and EDS mappings of an MWNT synthesised without sulphur at 240 °C). It is known that the following pyrolytic decomposition of nickelocene occurs even at room temperature;  $\text{Ni}(\text{cp})_2 \rightarrow \text{Ni} + \text{cp} + \text{cp}$  and  $\text{Ni}(\text{cp})_2 \rightarrow \text{Ni} + (\text{cp})_2$ , and the pyrolysis of nickelocene into nickel atoms and (cp) rings is greatly enhanced with an increase in the temperature [43]. It is therefore supposed

Download English Version:

<https://daneshyari.com/en/article/230598>

Download Persian Version:

<https://daneshyari.com/article/230598>

[Daneshyari.com](https://daneshyari.com)