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CVD synthesis of carbon nanotubes using a finely dispersed cobalt catalyst and their use in double layer electrochemical capacitors

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Abstract

Carbon nanotubes (CNT) were obtained by chemical vapour deposition (CVD), decomposing turpentine oil over finely dispersed Co metal as a catalyst at 675 °C. Scanning electron microscope (SEM) and transmission electron microscope (TEM) images reveal that the nanotubes are densely packed and of 10–50 nm in diameter. The XRD pattern of purified CNT shows that they are graphitic in nature. Resistivity measurements of these CNT indicate that they are highly conducting. Hall measurements of CNT reveal that electrons are the majority carriers with a carrier concentration of 1.35×10^{20} cm^{-3}. Cyclic voltammetry (CV) and constant current charging/discharging was used to characterise the behaviour of electrochemical double layer capacitors of purified CNT with H_2SO_4. For CNT/2 M H_2SO_4/CNT, a capacitance of 12 F g^{-1} (based on the weight of the active material) was obtained.

Keywords: Carbon nanotube; CVD; Synthesis; Double layer capacitor; Turpentine oil

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1. Introduction

Preparation of carbon nanotubes (CNT) from C_{60} by Curl, Kroto and Smalley [1] gave a great appraisal in the field of development of CNT. In recent years, they have generated tremendous interest from both fundamental and applied perspectives [2,3]. CNT possess many unique properties such as high mechanical strength [3,4], capillary properties [5] and remarkable electrical conductivity [6,7], suggesting a wide range of potential applications. CNT has been proposed as material for storage of hydrogen [8], supercapacitors [9], etc. CNT have been synthesised by various methods like arc discharge [10], laser vaporisation [11], and plasma-enhanced [12] or thermal chemical vapour deposition (CVD) [13]. Among these methods, CVD has been more popular because by this method CNT can be synthesised with high purity and in high yield, including textured assemblies, if catalysts are used (e.g. vertical alignment).

Hydrocarbons such as methane [14], acetylene [15], benzene [16], polyethene [17] etc., being derived from fossil fuels, have been used as precursors for CNT. If a high production volume is envisaged (e.g. for reinforced composite building materials), the use of natural precursor sources might be an advantage. Sharon et al. have obtained various forms of graphitic carbon by pyrolysis of camphor, like fullerenes [18], nanotubes [19], glassy carbon [20], spongy beads [21], and diamond like carbon [22].

Various carbonaceous materials have been discussed as electrode materials in electrochemical double layer capacitors. With certain carbon preparations of surface area up to 2000 m^2 g^{-1}, capacities as high as a few hundred F g^{-1} have been obtained [23,24]. CNT, due to their high specific surface area, are candidates for such "supercapacitors" [25,26], but also due to fact that electrodes made of CNT can have a pore structure determined by the open space between entangled fibres

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and therefore a high accessible surface area, unobtainable with other carbon materials [25].

In this paper we report on the preparation of CNT by low temperature (675 °C) CVD of turpentine oil (derived from the resin of pine trees). One point of interest was to see whether abundant and regular nanotube growth can be brought about using a finely divided Co catalyst, and whether such a catalyst can be prepared by sudden thermal decomposition of a metal salt solution containing urea. Another point concerned the characterisation of CNT obtained in this way, and of an electrochemical double layer capacitor based on such CNT.

2. Experimental

Co metal catalyst powder was prepared by rapid thermal decomposition of an aqueous solution of $Co(NO_3)_2$ (7.9% w/w) and urea (39.5% w/w) by sudden thermal decomposition at 600 °C. As the decomposition of urea is highly exothermic and large amounts of ammonia and carbon dioxide are liberated, the metal oxide is obtained in very fine form. The residue was reduced in H_2 at 500 °C for 3 h, yielding a very fine metal powder which was used as catalyst to grow CNT by CVD of turpentine oil. The CVD unit consisted of two furnaces joined side-by-side with a quartz tube traversing both of them (Fig. 1).

The first furnace (A) was used to vaporise turpentine oil and the second (B) was used to pyrolyse the vapours carried over from A by a stream of Ar gas. A quartz boat (E) with 2 ml of turpentine oil was placed in furnace A, maintained at 200 °C. The temperature of the furnace (B), containing a quartz boat (D) with the catalyst (Co particles), was maintained at 675 °C. After pyrolysis, the reaction mixture was collected from the boat and refluxed with concentrated HNO_3 for 24 h under constant stirring at 80 °C, in order to separate the CNT from the Co catalyst powder and most of the amorphous carbon. After that, the CNT were filtered off and washed with distilled water. This gave Co particle free nanotubes which were finally heated in air at 400 °C to eliminate any residual amorphous carbon.

For topological characterisation, a Philips CM-200 transmission electron microscope (TEM) and a Philips 1790 X-ray diffractometer, employing Cu–K_α radiation, were used. 1 mm thick pellets (1.2 cm diameter) were prepared to study the electrical properties of the material. For resistivity and Hall effect measurements, the Van der Pauw configuration was used. The resistivity of the pellets was measured between room temperature and 500 °C in argon. The series resistance of complete cells was measured with an LCR meter (Hewlett–Packard). For electrochemical studies a Pine AFRDE4 potentiostat was used. A cell of configuration CNT | H_2SO_4 || H_2SO_4 | CNT sandwiched between two pieces of carbon paper was assembled between Perspex plates (Fig. 2).

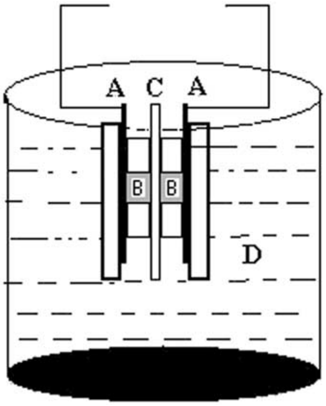


Fig. 2. Schematic diagram of a CNT based double layer capacitor. A ... carbon paper, B ... CNT, C ... separator (filter paper soaked with electrolyte), D ... electrolyte; the assembly is held together by two Perspex plates.

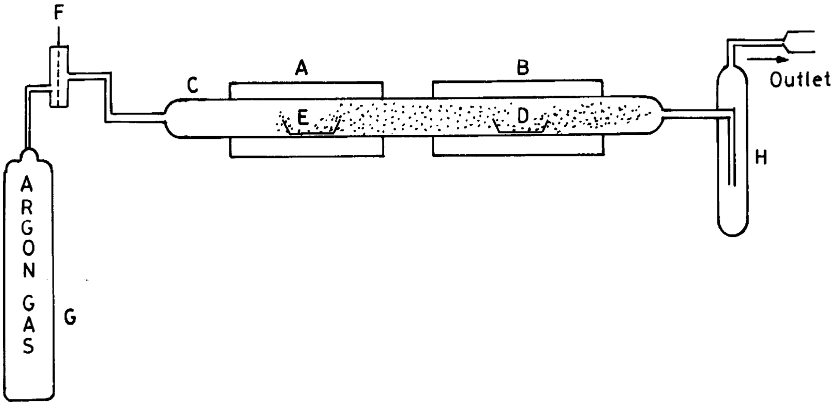


Fig. 1. Schematic diagram of the CVD setup. A ... vaporising furnace, B ... pyrolysing furnace, C ... quartz tube, D ... quartz boat with catalyst, E ... quartz boat with precursor, F ... flow regulator, G ... gas cylinder, H ... gas bubbler.

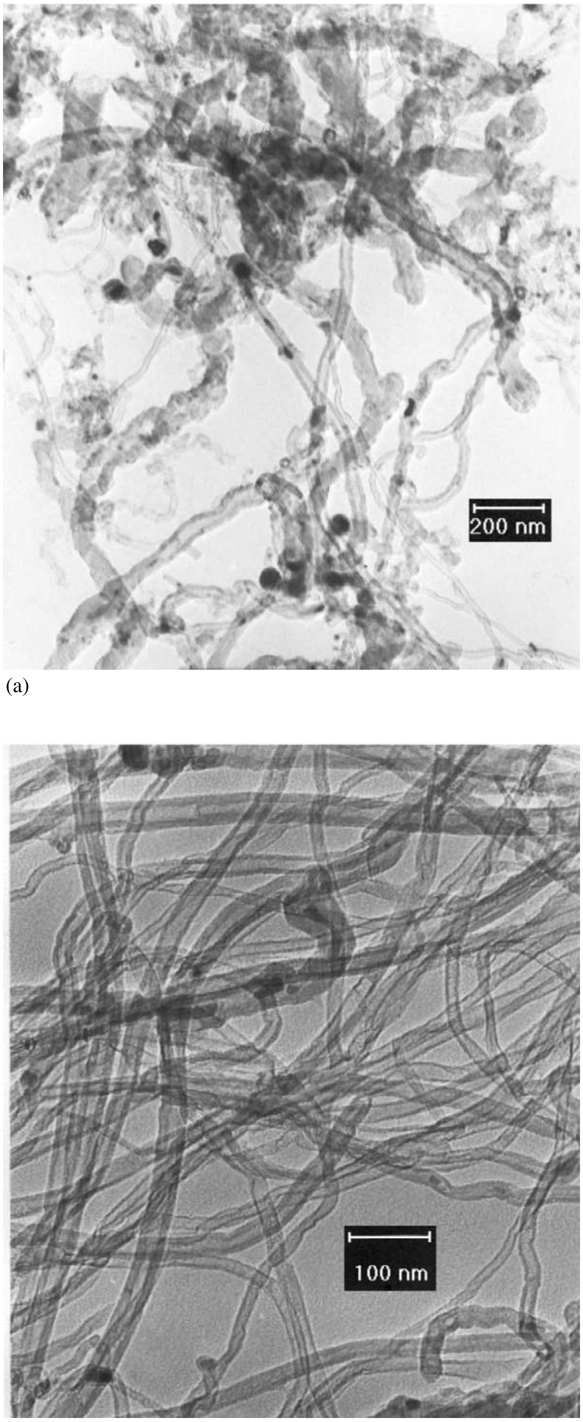
3. Results and discussion

CNT growth is known to be catalysed by very small particles of metals such as Ni, Co, Fe [27]. We therefore devised a new method for obtaining a catalyst preparation with a high content of such particles. The rapid thermal decomposition of metal salt solutions in the presence of urea yielded a very fine oxide powder. In the present case, this residue was identified as Co_3O_4 by XRD analysis and led, upon reduction, to the finely divided Co powder. CVD growth of CNT occurred with a high yield using this catalyst.

TEM images of CNT films are shown in Fig. 3. Fig. 3a shows the CNT before purification. Here, globular particles at the end of the CNT are the Co catalyst, being absent in the purified material (Fig. 3b).

It can be seen that the diameter of a CNT is around 10–50 nm. All results described below were obtained for purified CNT as described above. An X-ray diffraction pattern of purified CNT is shown in Fig. 4, revealing characteristic graphitic peaks at 2θ values of 26.66° (002) along with other planes (102) at 50.130, (100) at 42.530, (101) at 43.315 and (004) at 54.885°. In addition, the reflection at $2\theta = 5.78°$ suggests the presence of a small amount of single wall nanotubes as stated by Yosida et al. [28]. The small peaks at 33.5 and 39.99° can be attributed to (110) and (112) graphitic planes. Although there may be small impurities remaining (unidentified minor broad peak at 36°), the quality of the material was considered good enough for employing it in a capacitor: prolonged purification leads to extensive loss of material, which would not be practical for an application. On the other hand, unpurified material gave quite unsatisfactory results (more than ten times lower capacities).

Hall measurements of CNT pellets were carried out to ascertain carrier type, mobility and carrier concentration. The material itself cannot precisely characterised in this way, as individual CNT cannot be measured. However, a rough estimation for pellets made of CNT can give some useful information: electrons were found to be the majority carriers with a concentration of around 1.4×10^{20} cm^{-3} taking into account the macroscopic dimensions of the pellets. The temperature dependence of the resistivity between room temperature and 700 °C shows a small linear decrease in the conductivity with increase of temperature indicating semiconducting nature of the prepared carbon. The room temperature resistivity was found 0.024 Ω cm (about 20 times higher than graphite, but low enough for CNT to be used in an electrochemical device).



(a)

(b)

Fig. 3. TEM images of the CNT before (a) and after (b) purification.

Junctions of CNT with aqueous H_2SO_4 solution were prepared in order to study the electrochemical properties of the material. The device used is outlined in Fig. 2. The CNT, contained in a small compartment, are soaked throughout with the electrolyte before mounting of the device leading to a slightly compressed solid/liquid pellet. For initial characterisation of this new CNT preparation, we gave preference to this configuration instead of using a solid pellet including filler. Nevertheless, some experiments with PVA as filler were carried out—results not shown—and found promising, although showing a change of characteristics with time (for a period of several weeks). We tried to obtain information about the capacitance of the junc-

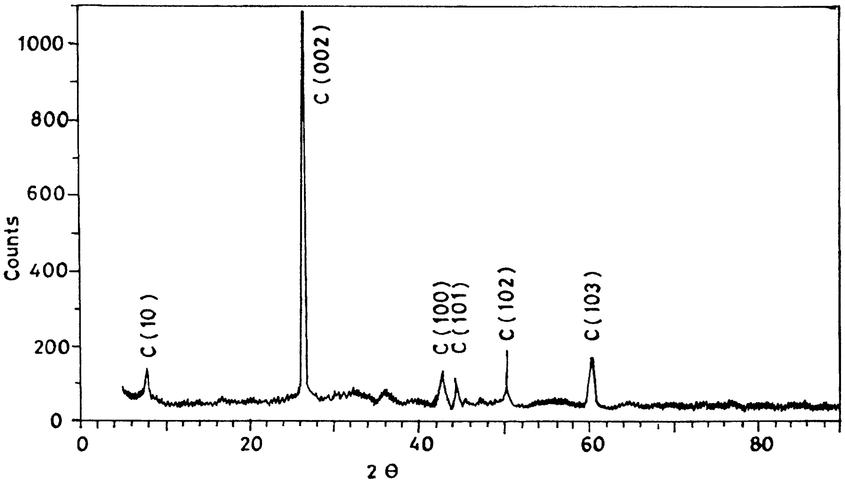


Fig. 4. XRD pattern of CNT.

tion from cyclic voltammetry (CV). From a potentiodynamic sweep, the capacitance (C) of any capacitor can be obtained by considering that C equals dQ/dU and the scan rate (s) is dU/dt. As the charging current, i, is dQ/dt, C can be expressed as

$$C = i/(dU/dt) = i/s \qquad (1)$$

For a cyclic scan, one half of the difference between forward scan and backscan currents is taken. For an electrode, i.e. a conductor/electrolyte junction, the double layer capacitance, C_{dl}, can be estimated in this way, if Faradaic currents, or pseudocapacitance, are absent. Otherwise, the dependence of i on scan rate shows a more complex behaviour, which is actually observed for cell voltage excursions beyond 0.4 V. A serial of typical CVs of CNT/2 M H_2SO_4 at different scan rates, are shown in Fig. 5.

In the inset, the currents at 0 V are plotted as a function of scan rate, assuming there is least contribution of Faradaic reactions at this voltage, however present. The plot shows a linear dependence of current on scan rate for high scan rates. At low scan rates, a sublinear dependence is observed. This is the expected behaviour for Faradaic currents when diffusion kinetics are involved, but also for the distributed nature of a porous electrode. In the here investigated samples, the pores in the electrode are interconnected spaces filled with electrolyte. These spaces are large compared with the dimension of the nanotubes, so that electrolyte access will be easier than in the case of activated carbon containing extremely small pores which are difficult to access. Nevertheless, for the present case, both, porosity and Faradaic reactions, can contribute to the observed behaviour (below, we shall show further evidence for the presence of the latter). If the high frequency response is mainly representative for the double layer capacitance of the device, the lower limit of capacitance may thus be estimated from the constant slope at the higher scan rates (in fact, a scan rate of 100 mV s^{-1} formally corresponds to operation of the device at 1/16 Hz). A value of 0.12 F was obtained under these conditions, corresponding to a specific capacitance of 12 F g^{-1} based on the total weight of active material in the two electrodes. Peaks observed in CVs with higher scan reversal voltages (Fig. 6) hint to electrochemical oxidation of the CNT, a fact well known for carbon materials [23], or redox reactions of yet unidentified surface active centres already present in the here presented CNT preparation, which might be suppressed by further pretreatment steps.

To confirm the capacity measurement through CV and to get information of the temporal behaviour, using a generally adopted test protocol, we also performed galvanostatic charging experiments. From Eq. (1), the cell voltage is expected to be a linear function of charging time. Constant currents of 1, 2, 4, and 8 mA yielded a typical charging/discharging behaviour of a capacitor (ideally a “/\/\/\. . .” shaped voltage response). An example with current inversion voltages of 0.4 and −0.4 V is shown in Fig. 7.

From the absolute value of the slopes of the voltage–time behaviour a capacitance of 0.1 F was again obtained. However, the slope decreased when approaching the reversal potentials. At higher current inversion voltages or at lower charging currents, “slower” components were gaining importance. The former is related to pseudocapacitances resulting from Faradaic reactions, while the latter is related to frequency dispersion of the capacitance due to the distributed nature of the electrodes. Such slow electron transfer reactions or Faradaic leakage currents represent a shunt to the double layer capacitance which also leads to the observed rapid self-discharge. As double layer capacitance and pseudo-capacitance are in parallel, use of this additional pseudo-capacitance as charge backup of the fast double layer capacitance can only be made if these

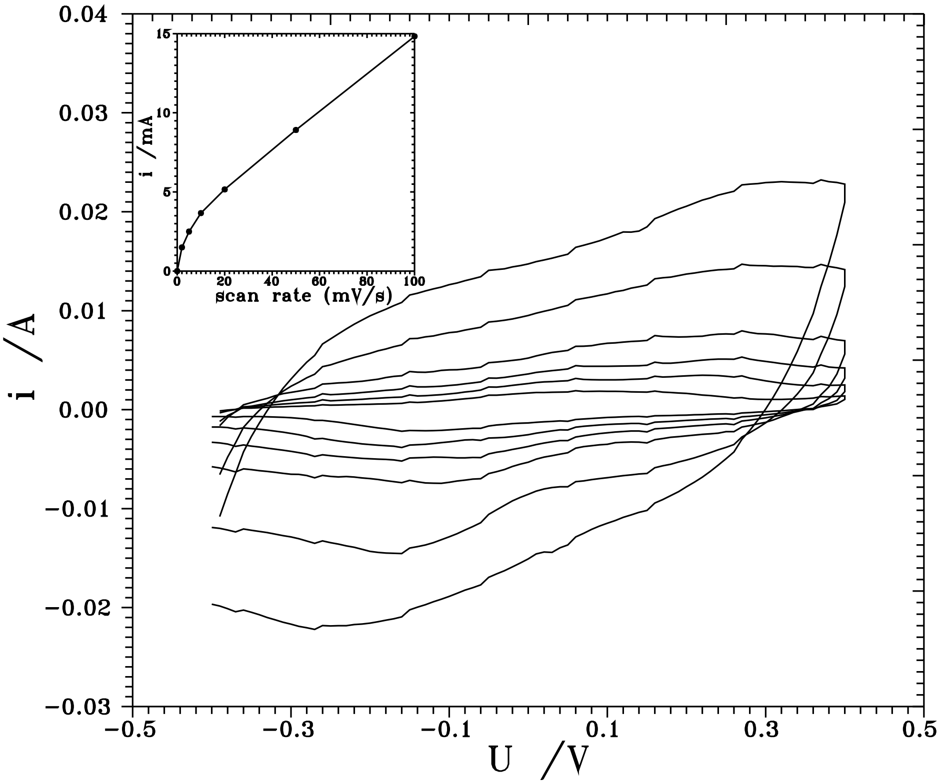


Fig. 5. CV of CNT based capacitor (5 mg per electrode) in 2 M sulphuric acid at scan rates of 2, 5, 10, 20, 50, and 100 mV s^{-1} (increasing currents); inset: dependence of current at 0 V on scan rate.

processes are reversible (a fact that has also been stated earlier [26]), which did not seem to be the case here. This can be seen from voltage step experiments: total charges of up to 0.8 C were found by integration of the i–t behaviour upon a voltage step from 0 to 0.4 V. The corresponding capacitance exceeds the one estimated

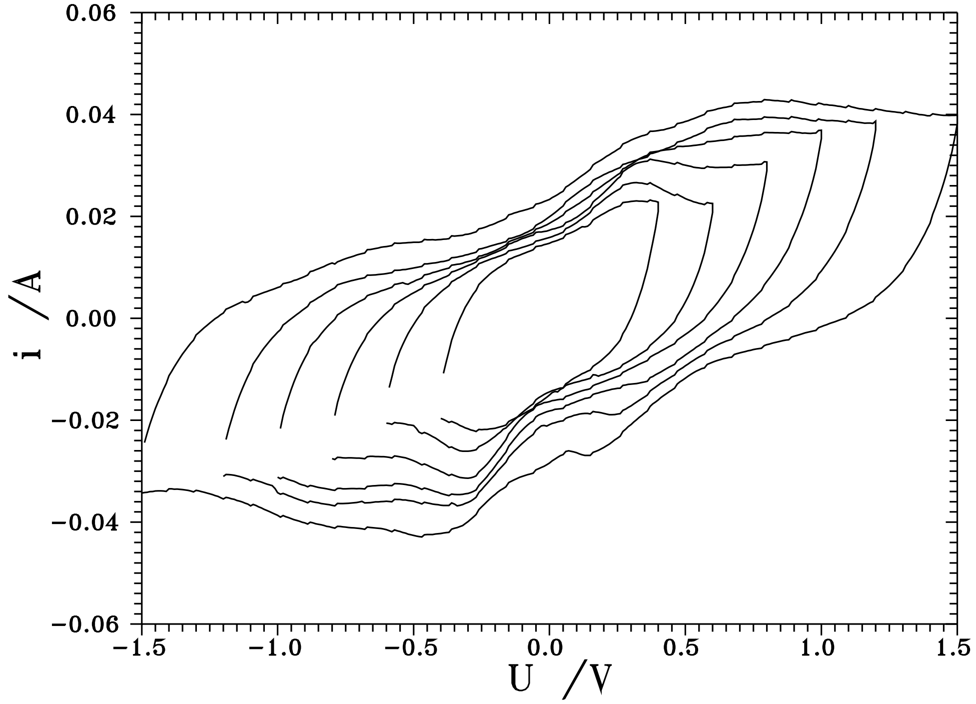


Fig. 6. CV of CNT in 2 M sulphuric acid with different scan reversal potentials; weight of electroactive material ... 2 × 5 mg; scan rate ... 200 mV s^{-1}.

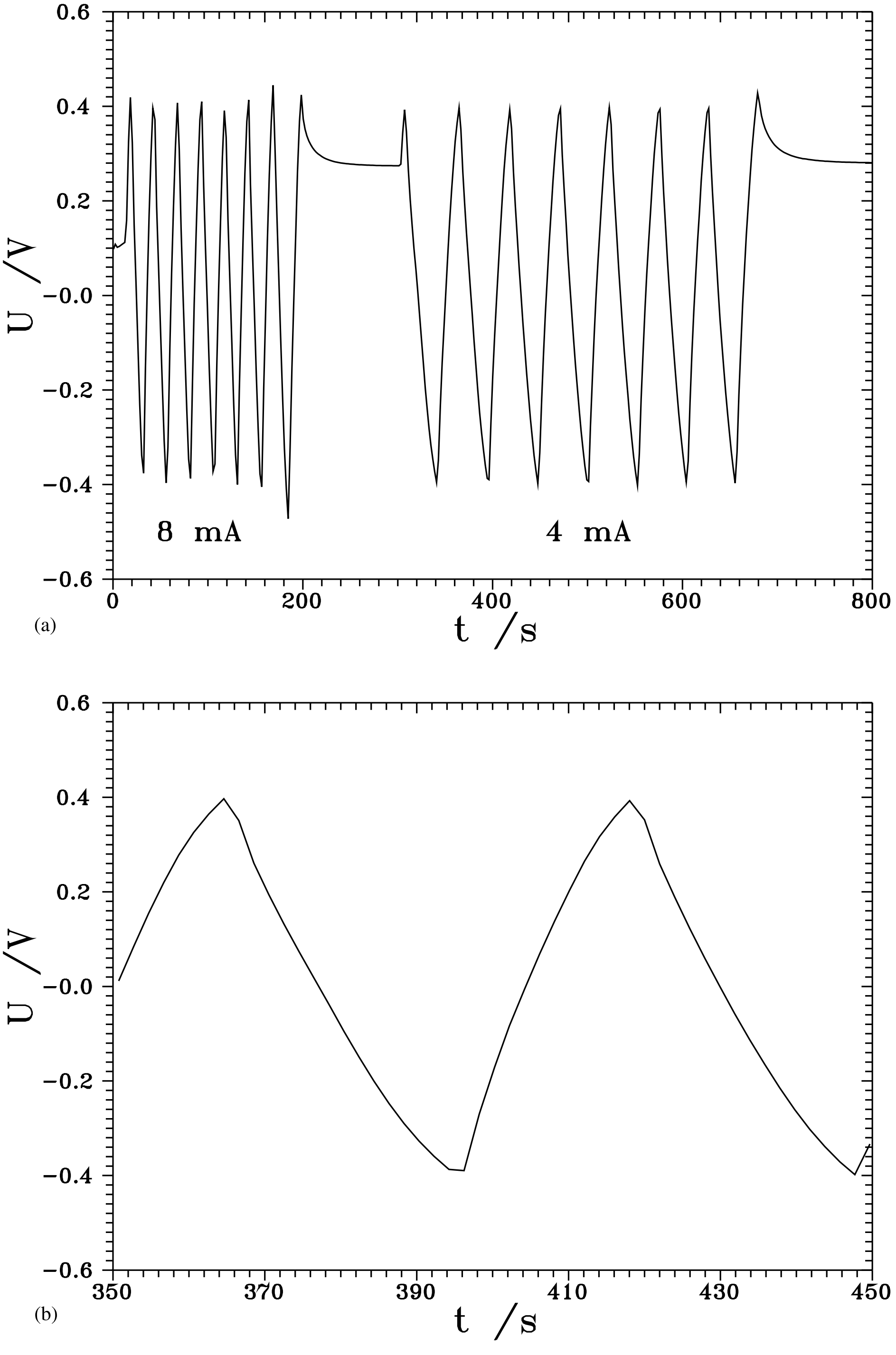


Fig. 7. Voltage–time dependence of the device shown in Fig. 2 for charging currents of (a) 8 and 4 mA, (b) expanded view for 4 mA; weight of electroactive material . . . 2 × 5 mg, 2 M sulphuric acid.

from CV or current cycling by a factor of ten. Upon stepping back from 0.4 to 0 V, however, only 0.06 C were recovered, corresponding to the double layer capacitance calculated from CV.

Table 1 resumes experiments carried out with cells made with different weights of electrode material. The capacitance depends on the amount of active material, as expected, and the specific capacitance is around 12 F g^{-1}.

The table shows fairly good agreement between capacitance measurements by CV and by galvanostatic step experiments, with the values obtained from CV being slightly lower (as expected from the discussion of the CV results above). Cells with 2 M sulphuric acid

Table 1
Capacitance of cells with CNT electrodes of 2.5 and 5 g in different media

Method	[H_2SO_4] (M)	CNT weight (total g)	Capacitance (F)	Specific capacitance (F g^{-1})
CV	0.1	0.01	0.085	8.5
Galv.			0.125	12.5
CV	2.0	0.01	0.118	11.8
Galv.			0.139	13.9
CV	2.0	0.005	0.060	12.0
Galv.			0.063	12.6

CV ... by cyclic voltammetry, galv. ... by galvanostatic step cycling.

showed lower resistance (5 Ω) compared with cells with 0.1 M acid (9 Ω). However, the self discharge was found to be higher for the higher acid concentration, presumably due to more efficient catalysis of the Faradaic reactions. Complete self discharge occurred in about 100 s for this cell, and even led to polarity reversal of the device, depending on its history (previous scans, etc.). Somewhat higher capacitances have previously been found for CNT base capacitors (81 F g^{-1} at 10 Hz), however for much thinner electrodes, having undergone an unspecified process of "thermal crosslinking" [25], and for acetylene black containing, PVDF binder supported CNT electrodes (36–80 F g^{-1} [26]). However, our aim here was to characterise a new CNT material first in the absence of any additives.

From typical capacitance values around 20 μF cm^{-2} observed for carbon electrodes [24], a surface area around 100 $m^2 g^{-1}$ can be derived for the here evaluated CNT. Although "activated" carbon, having a large number of pores, shows values up to 2000 $m^2 g^{-1}$, some of the very small pores cannot be reached (filled) by the electrolyte, leading to much lower actual values of specific capacitance than estimated from the specific surface area. As CNT do not have such pores, it can be imagined that basically the total surface area can be made available for the double layer to develop. Still, some spreading of the material by an electrolyte impregnated filler may increase accessibility. However, interconnectivity of the CNT must not be lost. Experiments in this direction are presently under way, also with regard to a more practical (solid/semi-solid) implementation of the device.

4. Conclusion

A finely divided Co metal catalyst, synthesised by decomposition of cobalt nitrate in the presence of urea supported the abundant growth of CNT during pyrolysis of turpentine vapours. These CNT are highly dense and intrinsically n-type. They have a low resistance due to high carrier concentration (1.4×10^{20} cm^{-3}). Such low resistance CNT are attractive for electrochemical and electronic applications. In the here presented example, an electrochemical double layer capacitor was assembled and tested. Specific capacities of up to 12 F g^{-1} (based on the total weight of active material) were obtained for this device. Slow response at higher voltages and fast self-discharge hints to the occurrence of Faradaic pseudo-capacitance.

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