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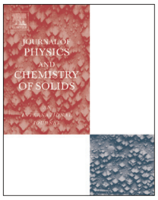

Electrical and morphological characterization of multiwalled carbon nanotubes functionalized *via* the Bingel reaction

Danijela V. Brković [a], Milka L. Avramov Ivić [b], Vesna M. Rakić [c], Luca Valentini [d], Petar S. Usković [a], Aleksandar D. Marinković [a,*]

[a] Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Serbia
[b] ICTM, Institute of Electrochemistry, University of Belgrade, Njegoševa 12, Belgrade, Serbia
[c] Department of Chemistry, Faculty of Agriculture, University of Belgrade, Nemanjina 6, 11080 Zemun, Serbia
[d] Department of Civil and Environmental Engineering, University of Perugia, Strada di Pentima 4, 05100 Terni, Italy

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ABSTRACT

Covalent sidewall functionalization of multiwalled carbon nanotubes (MWCNTs) has been performed using two approaches, direct and indirect cycloaddition through diethyl malonate, based on the Bingel reaction. The results revealed that functionalized MWCNTs demonstrated enhanced electrical properties and significantly lower sheet resistance, especially after electric field thermal assisted annealing at 80 °C was performed. The presence of 1,3-dicarbonyl compounds caused the surface of MWCNTs to be more hydrophilic, approachable for the electrolyte and improved the capacitance performance of Au/MWCNTs electrodes. The modified MWCNTs have been incorporated into nanocomposites by using solution mixing method with polyaniline and drop-casting resulting mixture on the paper substrate. The reduction in the sheet resistance with increasing the content of MWCNTs in the prepared nanocomposite films has been achieved.

1. Introduction

MWCNTs have attracted enormous attention due to unique characteristics resulting from their exceptional electrical, mechanical, chemical and structural properties [1]. In the last two decades considerable efforts have been made, to extend the possibility of their implementation in many fields of science and technology. However, the application itself has been restricted by inert and inactive nature of the surface of carbon nanotubes, low dispersibility in organic and aqueous solvents caused by the strong intermolecular van der Waals interaction between tubes.

Functionalization of carbon nanotubes is an effective way to overcome the solubility limitations, provide a homogeneous distribution in a variety of mediums and prevent tendency of nanotubes toward agglomeration. The introduction of functional groups, by covalent bonding and non-covalent wrapping surfactant molecules or polymers, changes the physical properties of nanotubes. These changes have especially been expressed in terms of dispersibility and electronic properties. Electronic properties of MWCNTs have been correlated with their structure and the covalent functionalization affects their ability to be in semiconducting and conducting states within the same tube. Specific electronic properties of carbon nanotubes are partially inherited from a two-dimensional structure of graphene. Nanotubes are formed from a graphene sheet folded in one dimension SWCNTs shape (cyclic folding), [3,4] which, regarding their electronic structure, can be metals or semiconductors, depending upon their dimensions and chirality. The influence of different types of covalent functionalization, monovalent and divalent addition, on electrical conductivity of SWCNTs has been investigated [5]. The conductance of the monovalent functionalized nanotubes has been decreased with the increased concentration of groups on sidewalls, toward divalent added groups, which have not been considerably contributed to the disruption of electrical conductivity [5]. Despite the theoretical assumption, that electron transport may be expected through both the outer and inner shells of MWCNTs, it has been found that electron transport at low energies has been mainly carried out through MWCNTs outer shells. Improved electronic properties have been highly desirable in the fabrication of nanoelectronic devices, transistor applications, high frequency nanoelectronics, storage media, inkjet printing, field emission, paint technology, nanoscale array fabrications and biological sensing.

The Bingel reaction has been one of the most common direct addition used in fullerene chemistry, to give cyclopropanated fullerenes by a reaction of C_{60} with halogenated active methylene

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* Corresponding author. Fax: +381 11 3370387.
E-mail address: marinko@tmf.bg.ac.rs (A.D. Marinković).

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compounds in the presence of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) [6]. During last several years, only few studies of single-walled carbon nanotubes (SWCNTs) functionalized by the Bingel reaction [7–10] have been reported. The Bingel reaction on carbon nanotubes has been expected to proceed by an addition reaction of the bromo malonate generated *in situ* by base followed by intramolecular nucleophilic supstitution to generate the cyclopropane ring [7]. As reported by Coleman et al. [8] diethyl malonate has been attached on to the SWCNTs walls under the Bingel reaction conditions and detection of the functional groups using chemical markers for AFM visualization has been performed. Worsley et al. [9] demonstrated that diethyl malonate groups, present on the surface of SWCNTs can arrange in very regular patterns that may be explained by long-range induced reactivity. This phenomenon has been related to their electronic structure, geometry of nanotubes, the degree of functionalization and nucleophilic reaction mechanism [2]. Benzyl 2-ethylhexyl malonate has been introduced on the surface of SWCNT as presented Umeyama et al. [10]. They emphasized the necessity of pretreatment procedure, which includes the oxidation and formation amide functionality on sidewalls, followed by the Bingel modification. Fernandes et al. [11] reported functionalization of MWCNT under Bingel reaction condition. The introduction of diethyl malonate followed by amidation with cysteamine on the surface of MWCNTs, and immobilization of Au nanoparticles, resulted in a nanohybrid for catalytic applications [11].

Polyaniline (PANI) doped with protonic acids is one of the most studied intrinsically conducting polymers [12,13]. The addition of MWCNTs inside polyaniline matrix has been used in order to improve the efficiency of electron transport and obtain conductive nanocomposites. Formation of conductive MWCNT–PANI networks offers many advantages in the field of organic electronics. A significant number of articles reporting fabrication and application of MWCNT/PANI films for supercapacitors, fuel cells, photovoltaic cells, sensors, and actuators have been published [14–16].

Herein, we present functionalizaton of MWCNTs *via* the Bingel reaction using 1,3-dicarbonyl derivatives as active methylene compounds. Nanomaterials were modified with different heterocyclic (structural) functionalities in order to change surface properties and morphology of graphitic surface. Two modification approaches have been applied for MWCNTs functionalizaton. The first approach was based on the direct addition of brominated 1,3-dicarbonyl derivatives (barbituric acid, dimedone, diethyl malonate and 2,2-dimethyl-1,3-dioxane-4,6-dione), and the second approach consisted from two steps: MWCNT has been firstly modified by diethyl malonate following, in second step, by their subsequent cyclization to barbituric and thiobarbituric acid. The characterization of functionalized nanomaterials was performed in order to get information on the morphology, dispersibility and wetting properties. Capacitance of electrochemical interfaces was measured by cyclic voltammetry. The effect of electronic structure of modified MWCNTs on electrical properties of conductive thin films formed from carbon materials and polyaniline (MWCNTs/PANI) was also discussed.

2. Experimental

MWCNTs (Sigma-Aldrich) prepared by a chemical vapor deposition (CVD) method were used as received without purification. The purity of MWCNTs was more than 95% and the outer and inner diameters were 20–30 and 5–10 nm, respectively, the length was between 5 and 200 μm and the specific surface area was 40–600 m^2/g. Reagents and solvents were used as received. Cyclic 1,3-dicarbonyl compounds: barbituric acid (pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione), thiobarbituric acid (2-thioxodihydropyrimidine-4,6(*1H*,5*H*)-dione), dimedone (5,5-dimethylcyclohexane-1,3-dione), and 2,2-dimethyl-1,3-dioxane-4,6-dione were synthesized according to the literature procedure [17–19]. All other chemicals and MWCNTs were purchased from commercial suppliers Sigma and Fluka, p.a. grade.

2.1. Preparation of the functionalized MWCNTs

Preparation of the bromo derivatives of barbituric acid, dimedone, and 2,2-dimethyl-1,3-dioxane-4,6-dione was performed according to previously established procedures [20–22]. MWCNTs were suspended in 1,2-dichlorobenzene and sonicated for 15 min at 35 kHz (240 W). The corresponding brominated derivatives of 1,3-dicarbonyl compounds (3.52 mmol) and 1 ml of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) were added to a suspension. This mixture was then sonicated for 10 h at 60 °C in an ultrasonic bath under inert atmosphere. Reaction mixture was allowed to cool down to room temperature, filtered through a 0.05 μm PTFE membrane and washed with 50 ml of 1,2-dichlorobenzene and 200 ml of ethanol. Finally, the materials were dried in the vacuum drying oven at 60 °C for 8 h and the desired products were obtained (Fig. 1a): MWCNTs modified with barbituric acid (**b1-MWCNT**), dimedone (**d-MWCNT**), diethyl malonate (**dem-MWCNT**) and 2,2-dimethyl-1,3-dioxane-4,6-dione (**m-MWCNT**).

In the second approach, the surface of MWCNTs was firstly modified by diethyl malonate (**dem-MWCNT**), following a previously described procedure. The **dem-MWCNT** were added to a solution of sodium (30 mg) in absolute ethanol (3 ml), followed by the addition of dry urea (0.079 g) dissolved in 3 ml of hot (70 °C) absolute ethanol. The mixture was refluxed for 7 h on an oil bath heated to 90 °C. After the reaction was completed, 2 ml of hot water (50 °C) was added and then hydrochloric acid to attain pH 3. The suspension was cooled, the product filtered off through a 0.05 μm PTFE membrane and washed with 5 ml of ethanol. The resulting product (**b2-MWCNT**) was dried in the vacuum drying oven at 60 °C for 8 h. The cyclization of diethyl malonate, present at **dem-MWCNT** surface by using thiourea (0.1 g) instead of urea to thiobarbituric acid to obtain **t-MWCNT** was carried out in the same manner as for **b2-MWCNT** (Fig. 1b). The structures of the introduced moieties are given in Table S1.

2.2. Preparation of the conductive nanocomposite films

Preparation of PANI was performed according to previously established procedure [23]. Conductive films were prepared by mixing of functionalized MWCNT with PANI in a mixture of *N*-methyl-1-pyrrolidone and *N*,*N*-dimethylformamide (1:1). The weight percent of functonalized MWCNT in a polymer matrix PANI was varied: 2 wt%, 5 wt%, 10 wt% and 20 wt%. The films (surface area of 1 cm^2) were fabricated by drop-casting dispersion on the paper substrate, using the Teflon mold and a copper mask and pelletized 2 min under pressure of 10 MPa for 2 min.

2.3. Characterization of MWCNTs

Fourier-transform infrared (FTIR) spectra were recorded in the transmission mode between 400 and 4000 cm^{-1} using a BOMEM (Hartmann & Braun) spectrometer with a resolution of 4 cm^{-1}. MWCNTs were pressed into a pellet with potassium bromide (1% by weight in KBr pellet) and scanned. Elemental analyses were performed using a VARIO EL III Elemental analyzer. Hydrophobic surface and specific surface area of MWCNTs were determined by using UV method (Shimadzu UV1700 spectrometer) and Brunauer–Emmett–Teller (BET) method, respectively.

On-line thermogravimetric–mass spectrometry analyses (TG–MS) was used to study the gases evolved during temperature-