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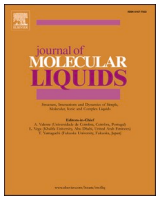

Ultra-fast mechanochemical strategy to obtain stable colloidal dispersions of MWCNT in hydrophilic media: Never has been so easy

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ABSTRACT

In this paper, we present a new protocol that allows the dispersion of multi-wall carbon nanotubes (MWCNT) in the form of stable colloids in a hydrophilic medium up to concentrations of ca. 0.06 % (w/w). The strategy involves using a combination of mechanochemical treatment and surfactants. In this study, we processed MWCNTs with surfactants in a ball mill without using any solvents. The mechanochemical treatment consists of processing mixtures of MWCNTs (0.35 g) with different surfactants (4.5 g of CTAB, 3.6 g of SDS and 4.5 g of F127 as cationic anionic and neutral surfactants, respectively) in a ball mill for only 20 min at 300 rpm. The resulting black powder is then used directly to prepare dispersions in hydro-alcoholic media, which maintain colloidal stability for at least 25 days. Although various strategies for dispersal have been proposed in the literature, many involve time-consuming and multi-step processes with low yields. The MWCNTs modified non-covalently using our protocol are synthesised in a single step with a 100 % yield without any loss of reagents. MWCNT have shown potential in many emerging applications of great interest. Its use necessarily implies the achievement of a good dispersion in different solvents, and this aspect, in the case of hydrophilic media, still does not have a satisfactory answer. The absence of solvent during the mechanochemical treatment is the key aspect of our strategy. This small change represents a significant improvement. We demonstrate the outstanding stability of the obtained suspensions and the preservation of the nano-/microstructure of the MWCNTs, which remains unaltered during their preparation. Furthermore, using environmentally friendly solutions for dispersion makes this protocol a Green Chemistry approach.

1. Introduction

The attribution of the discovery of carbon nanotubes (CNTs) is not without controversy [1]. Although Radushkevich and Lukyanovich published the first Transmission Electronic Microscopy (TEM) images showing the hollow structure of carbon filaments in 1952 [2], their work was largely forgotten. For this reason, the rediscovery and enhancement of CNTs occurred almost 40 years later thanks to the work of Iijima [3] and, this time; they immediately aroused the interest of the scientific community, which, according to the number of articles published, evolved exponentially until the year 2010 and has maintained it until today with around 50.000 publications. To a large extent, this popularity is due to the remarkable structural, mechanical, and electromechanical properties [4,5] that make CNTs promising candidates for a large variety of emerging applications [6] in electronics [7], analysis [8], medicine [9], catalysis [10], sensors [11,12], energy [13,14], and engineering applications [15] among others.

Although advances in production have enabled the availability and commercialisation of CNTs (both as SWCNTs and as MWCNTs), their price as high-purity materials is, in most cases and for specific applications, cost prohibitive. MWCNTs can be produced on a large scale utilising chemical vapor deposition (CVD) [16]. MWCNTs are non-dispersible in various solvents due to strong van der Waals interactions that hold them together, forming packages [17]. This handicap is compounded when dispersion is required in hydrophilic media. There is then a significant decrease in the overall yield of usable

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material. For specific applications, dispersibility in hydrophilic media is mandatory. These applications include those in environmental, remediation and medicine, such as biosensors, drug delivery, and theragnostic materials. Furthermore, for most MWCNT-based materials, their dispersion (generally in hydrophilic media) is the starting point for modification or combination with other solids to produce final materials/composites with the desired properties. Thus, in many cases, we can consider that the accurate starting carbonaceous reagents are nanofluids, stable suspensions of MWCNT as micro/nanoparticles [18]. To achieve this goal MWCNTs can be modified by strategies involving covalent or non-covalent functionalisation [19–22]. The chemical covalent functionalisation is mainly based on oxidative treatments. As a general rule, the oxidation of MWCNT produces open tubes with functional groups containing oxygen (predominantly carboxylic acid) both on the side wall and on the ends of the tube. These groups can be used as chemical anchors for subsequent sequential derivatisations. On the other hand, non-covalent functionalisations occurs through van der Waals π-π forces and interactions by adsorption or coating with polynuclear aromatic compounds, surfactants, polymers, or biomolecules. The main advantage of the non-covalent functionalisation of CNTs over covalent functionalisation is that the former can introduce chemical functionalities on the surface of CNTs without affecting their structure and electronic network. The latter strategy focuses on the nanotube-molecule interaction and the colloidal stability of the formed adducts.

Although mechanochemistry (specifically the use of ball mills) is a classic tool in areas related to chemistry, such as the ceramics industry, it must be recognised that, despite its simplicity, it has not aroused much interest in other areas of chemistry. There seems to be a particular resurgence of mechanochemistry in various fields of chemistry, such as the preparation of catalysts, among others [23,24]. Pan et al. published in 2002 the first SWCNT dispersion strategy by grinding a mixture of them and KOH in a ball mill for 2 h [25]. Subsequently, the method required successive washings to lower the pH and remove excess potassium hydroxide. Chen et al. later adopted this strategy for the MWCNT dispersion [26]. In both cases, the process results in the oxidation of the CNTs and the formation of hydroxyl groups on them. The result is easily dispersible CNTs in hydrophilic media. However, in a stricter sense, the result is not a "physical" modification. It is rather a functionalisation with OH groups, which can alter the nature of the CNT in terms of its electronic structure. Subsequent work using ball mills or traditional mortar grinding has disentangled the CNT aggregates. Still, additional post-treatments have been necessary to achieve a certain degree of dispersion, involving stages of sonication, centrifugation, successive washes, and surfactants or mineral species [27–30]. In short, multi-step processes require long synthesis times. The combined use of these techniques implicitly indicates that a certain amount of leaching occurs in each stage. The result may be an excellent stable dispersion of CNT, but a significant part of an expensive material has been lost along the way. As a matter of fact, in some cases, only the supernatant suspension is used. A recent review shows that the most widely used methods for dispersing CNTs and, ultimately, building materials or composites with properties of interest are mainly based on surfactants, prolonged ultrasound treatments and subsequent centrifugation [31].

In this work, we hypothesise that the mechanochemical strategy of a mixture of MWCNTs with surfactants (cationic, anionic, or neutral) can be a suitable approach to achieve a solvent-free process preparation of carbon nanotubes highly suspendable in hydrophilic media for very long periods without post-sonication or centrifugation steps.

2. Experimental procedures

2.1. Materials

The MWCNT employed in this work were used as received from Nanoamor (Nanostructured & Amorphous Materials, Inc.; Katy, TX 77494, USA). This reagent corresponds to a standard regular-length MWCNT with the following characteristics/specifications: purity (>98 %), outside diameter (30–50 nm), inside diameter (5–12 nm) and length (<10 μm). All the remaining synthesis reagents were analytically pure and were used as received from Aldrich (Merck Group, Darmstadt, Germany) (cetyl-trimethylamonium bromide [CTAB] (≥98 % (wt)), sodium dodecyl sulfate [SDS] (≥98 % (wt)), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) diacrylate [F127] (≥98 % (wt)) and ethanol (99 %)).

2.2. Method

Eight 1 cm agate balls, 0.35 g of MWCNT, and 4.5 g of CTAB (alternatively, 3.6 g of SDS or 4.5 g of F127) are introduced in an agate mortar and grounded for 20 min at 300 rpm in a single direction of rotation (Retsch S100 instrument). The resulting black powder is directly used to make the dispersions. To prepare the dispersions, 0.11 g of the MWCNT/surfactants composites, 10 mL of water, and 5.56 mL of ethanol are added into a vial; no additional processing steps are required. Samples disperse even without stirring. These concentration values coincide with those used in the Turbiscan and DLS measurements (514 mg/L (0.056 %(w/w)) in the case of CTAB and F127 and 626 mg/L (0.068 % (w/w)) in the case of SDS). Dealing with the surfactant concentrations, we can indicate that they are similar to or slightly higher than those employed in previous works [32], around 0.6 % by weight on the final dispersion.

For comparative purposes and to analyse the possible MWCNT degradation through the mechanochemical treatment 0.35 g of MWCNT were ground following exactly the above procedure in the absence of surfactants.

Finally, to verify the complete preservation of the MWCNT after the mechanochemical treatment (without altering the sp^2 hybrid state of the carbon atoms), the MWCNT/CTAB composite was washed with ethanol to remove the surfactant. Thus, 4.85 g of the MWCNT/CTAB mixture was suspended in 150 mL of ethanol and heated under reflux for 24 h. The resulting dispersion was centrifuged for 10 min at 10000 rpm. The supernatant solution was decanted, and the resulting black powder was again washed with ethanol, centrifuged, and dried overnight. This CTAB extraction process is then repeated. In this way, we recover the unfunctionalised MWCNT.

2.3. Characterisation techniques

The suspension behaviour was analysed by the Turbiscan technique, dynamic light scattering (DLS) and ζ-potential. A Turbiscan Lab® Expert equipment (Formulaction Scientific Instruments, France) was used at 25 °C for 25 days. The suspensions were introduced into 30 mL cylindrical glass vials to a height of approximately 35 mm. Transmittance and backscattering of a pulsed near-infrared light (λ = 880 nm) were recorded along the entire height of the sample. The size of the MWCNTs (commercial reagent and washes after applying the mechanochemical process in the presence of surfactant) were measured using a Malvern Mastersizer 2000 instrument (633 nm laser) equipped with the Scirocco 2000 accessory required for dry measurements. The measurements were carried out in triplicate, accumulating 10 s of background and 10 s of sample passing through the measurement cell. Determination of the aggregate size (MWCNT/surfactants) was carried out using a Malvern Nanosizer ZS instrument. (accumulation time = 192 s). ζ-potential (45 cycles/measurement; at pH around 6.5).

The MWCNT and the mixtures of MWCNT/surfactants were characterised through TEM, XRD, IR, Raman, electrical conductivity and Seebeck coefficient measurements. For electron microscopy analyses, the solid samples were dispersed in ethanol, placed onto a carbon-coated copper microgrid, and left to dry before observation. In the case of colloidal suspensions, a drop was placed on the microgrid and allowed to dry. TEM (transmission electron microscopy) images were acquired with a JEOL-1010 microscope operated at 100 kV. HRTEM (high resolution

transmission electron microscopy) images were acquired with a TECNAI microscope operated at 200 kV with a resolution of 0.24 nm. This microscope is equipped with a GATAN CCD camera and "Digital Micrograph" image acquisition and processing software. X-ray powder diffraction (XRD) was carried out using a Bruker D8 Advance diffractometer equipped with a monochromatic CuKα source operated at 40 kV and 40 mA. Patterns were collected in steps of 0.02° (2θ) over the angular range 5-80° (2θ), with an acquisition time of 25 s per step. The IR measurements were made with a Perkin Elmer Spectrum Two equipment, and 16 scans were acquired between 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. Raman analysis was carried out using a Horiba MTB XPlora Raman spectrometer with a laser light source of 532 nm. The scanning range was 375–3750 cm^{-1}, and three scans were collected. Electrical conductivity was measured using 4-probe technique, applying an intensity on the outer contacts and measuring the voltages in the inner ones with Keithley Sourcemeter 2636B. Seebeck coefficient was measured using a homemade set-up using a temperature controller TC300 connected to two peltiers and two thermocouples and Keithley Sourcemeter 2636B to measure the thermovoltage.

3. Results and discussion

3.1. Preparation of highly stable dispersions

Our strategy combines surfactants (CTAB, SDS and F127) and MWCNT with a ball milling treatment. The addition of surfactants is a simple, relatively inexpensive, and easy way to improve the dispersibility and stability of CNT suspensions. In addition, the ball mill method has some advantages, such as low installation cost, low energy consumption, and versatility. Innumerable combinations of chemical and/or physical strategies have been described in the literature to stabilise MWCNT suspensions in water [33]. Still, no case was the mixture of carbonaceous material and surfactant dry processed in a ball mill. This point is critical in our strategy. In addition, we adapted the ball milling conditions so that the length of the MWCNTs was not (significantly) reduced, and the pristine sp^2 hybrid state of the carbon atoms was preserved. For this reason, we use agate balls, which are among the softest (hardness in the range of 6.5–7 on the Mohs scale; about 1000 HV) and generate a meagre energy input. In addition, we use large balls with a diameter of 1 cm, a value that far exceeds the average size of the MWCNT, a mortar filling of 50 % by volume (to favour sufficient freedom of movement of the balls and the material), and rpm conditions relatively low (300 rpm) to reduce the number of impacts and avoid heating of the sample. This relatively low speed was also based on previous work on wet milling of MWCNTs, which showed that no significant reduction in nanotube length was observed up to 300–400 rpm [34]. Under these conditions, we minimise the impact forces (to preserve the length of the MWCNTs) and achieve sufficient frictional forces to mix the MWCNTs and the surfactant very intimately. The hydrophobic nature of the tails of the surfactants leads to the non-covalent functionalisation of the MWCNTs. It should be noted that, unlike other complex multi-step strategies that take a long time, our method produces in just 20 min a MWCNT@surfactant mixture, which can be easily dispersible in aqueous solutions with outstanding colloidal stability. In addition, the process is valid for cationic, anionic, and neutral surfactants, which allows the surface adaptation of the MWCNTs depending on their application or subsequent treatments to be carried out.

First, we want to highlight the extreme stability of the MWCNTs modified with the different surfactants. The Turbiscan optical device allows us to monitor and quantify the stability of the suspensions. This technique is considered the gold standard for analysing the stability of suspensions [33,35]. No changes in transmittance and backscattering

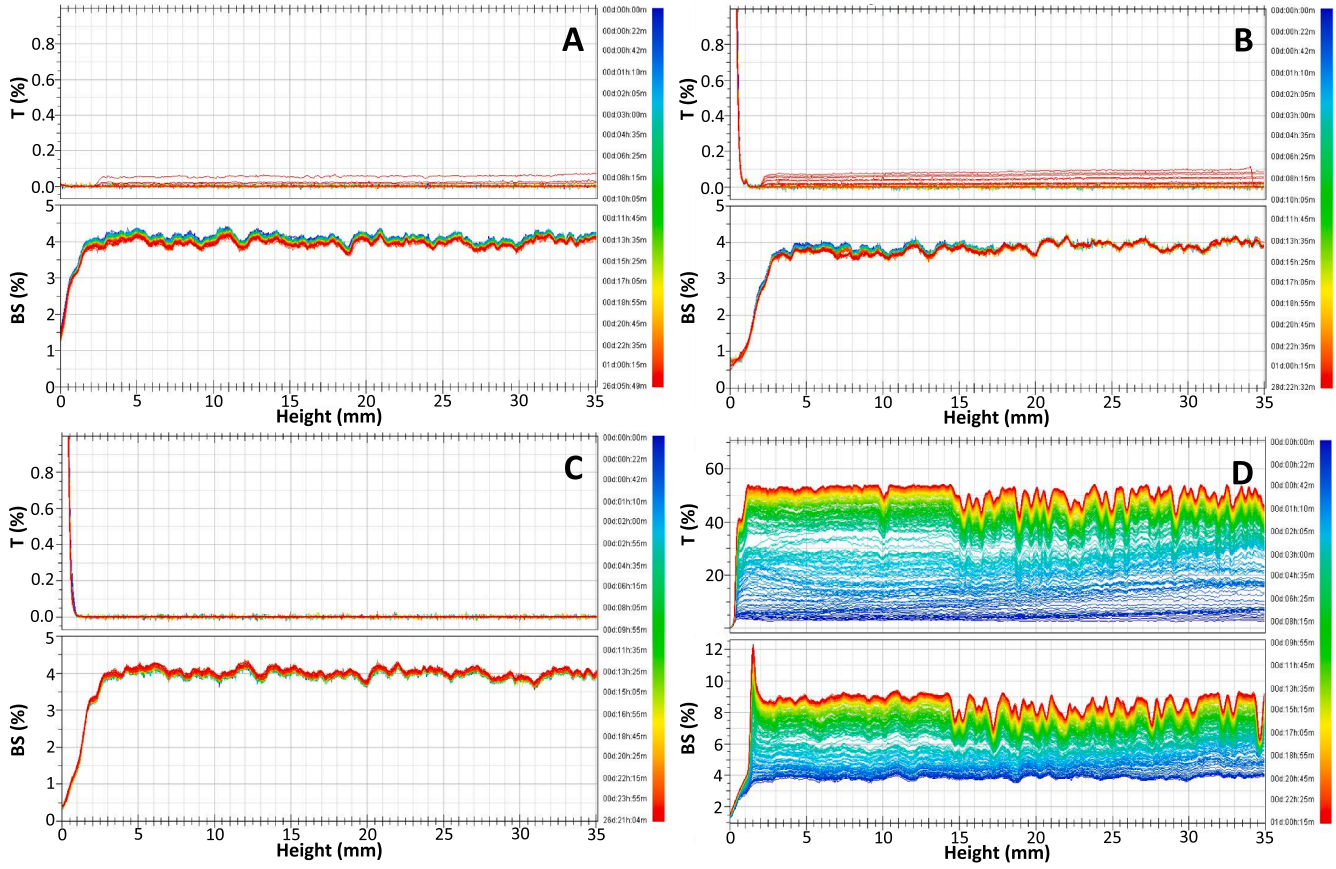

Fig. 1. Turbiscan transmittance and backscatter profiles of samples ground in the ball mill (A) MWCNT/CTAB, (B) MWCNT/SDS and (C) MWCNT/F127. For comparative purposes we shown the sample MWCNT/CTAB without the mechanochemical treatment (D).

measurements are detected over time (25 days) for all three surfactants with similar concentrations in MWCNT of ca. 0.06 %(wt) (514 mg/L in the case of CTAB and F127 and 626 mg/L in the case of SDS) (Fig. 1a to 1c).

Thus, we can indicate in an unquestionable way that no sedimentation, cream formation, flocculation, or coalescence phenomena are observed (they are completely non-existent). The measurement of MWCNT/CTAB mixed without the ball mill (Fig. 1d) shows significant changes quickly, consistent with rapid sedimentation. This phenomenon highlights the need for a mechanochemical treatment in order to obtain a stable colloidal dispersion of MWCNT/CTAB. The Video in the supporting information shows the differences in the dispersion of MWCNT/CTAB mixtures obtained with and without a ball mill in hydroethanolic media. The quantification and comparison of the measurement can be made from the evolution of the Turbiscan Stability Index (TSI). Fig. 2 shows that the TSI values are very low and do not evolve significantly over time. It is often difficult to compare the concentration of MWCNTs truly dispersed in previous work in the bibliography. Mechanochemical milling, ultrasonic treatments and surfactants are generally used in the strategies described. In some cases, a certain degree of sedimentation is described [36]. In other cases, further dilutions (up to a factor of 150) are required for the UV–vis spectroscopic study [37]. Clark et al. [32] analysing the MWCNT concentration after several filtration and centrifugation steps indicates that similar values, between 10 and 15 mg/L, are achieved for CTAB, SDS and F127. Other cases require non-commercial dispersants such as oligothiophene-terminated poly (ethylene glycol) [38]. The covalent functionalisation with –COOH groups allows the solubility values of 0.014 % (wt) and 0.05 % (wt) in polar and non-polar solvents to be achieved, respectively [39]. Thus, without covalent functionalisation, the concentrations of MWCNTs dispersed in aqueous solvents range from 0.02-0.04 % (wt). Thus, in addition to zero MWCNT losses, our strategy allows us to achieve highly concentrated carbonaceous dispersions (ca. 0.06 % wt). In summary, a composite is obtained in a single processing step using commercial reagents (MWCNT and surfactants), in which the nanotubes are modified only in a non-covalent manner within a short time frame of 20 min. This composite enables an increase in MWCNT solubility by producing stable colloidal dispersions in hydrophilic media for extended periods of time without the losses of MWCNT that occur in other multi-stage preparative strategies described in the literature. The video in the supplementary material demonstrates that the MWCNT/surfactant composite can be easily dispersed without additional protocols or stirring once prepared using the mechanochemical treatment.

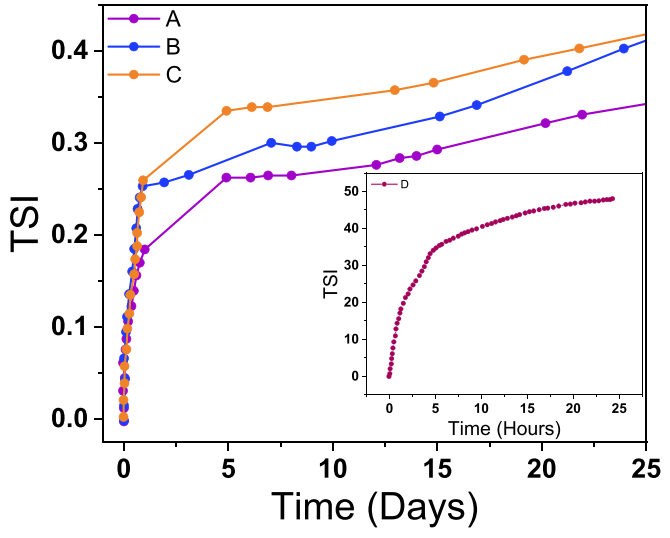

Fig. 2. TSI vs time of samples ground in the ball mill (A) MWCNT/CTAB, (B) MWCNT/SDS and (C) MWCNT/F127. For comparative purposes we have shown in the inset the sample MWCNT/CTAB without the mechanochemical treatment (D).

This excellent dispersion is achieved without morphological alteration of the MWCNTs. Our goal is to preserve its integrity. Fig. 3 compares the TEM images of the commercial starting material and that treated in the ball mill (without and with surfactants, under the same conditions described in the experimental procedure). The morphology in the form of aggregates or coils of nanotubes is preserved, and the lengths of the MWCNTs show a qualitatively similar homogeneity. (always less than 10 μm, according to the specifications of the commercial starting material). In conclusion, the mechanochemical treatment does not affect the nanotubes on a nano/micrometric scale. With the three surfactants, a significant decrease in nanotube aggregates is achieved with high homogeneous dispersion. In the case of surfactant F127, which has a higher molecular weight and size than CTAB and SDS, a slightly greater separation of MWCNTs is qualitatively appreciated. The crystallinity of the MWCNT is also not affected according to the XRD data (Figure S1).

Turbiscan and DLS are two complementary techniques in the study of nanomaterial dispersions. The suspensions should be stable to obtain accurate DLS measurements. We can quickly check this by seeing the correlation curves generated during the DLS measurement. Samples that exhibit high stability in the Turbiscan produce accurate correlograms and size results in the DLS. Conversely, unstable samples in the Turbiscan measurement yield poor correlograms and erroneous size measurements due to the particles not conforming to the Brownian motion model. DLS measurements are shown in Fig. 4. The three MWCNT samples were non-covalently functionalised with CTAB, SDS, and F127 and showed good dispersion, with polydispersity index (PDI index) values of 0.225, 0.124, and 0.415, respectively. The PDI index is a parameter to define the particle size distribution, which is expressed as a dimensionless number extrapolated from the autocorrelation function in photon correlation spectroscopy. PDI values < 0.7 indicate a good polydispersity, consistent with good preservation of the typical Brownian movement of stable colloidal systems [40]. In the case of the MWCNTs functionalised with CTAB and SDS, unimodal size distributions are obtained with hydrodynamic diameters of 320 nm (% Intensity = 93.7) and 198 nm (% Intensity = 100), respectively. These differences in size correlate qualitatively with the size of the surfactant molecules. In the case of the material modified with F127, two signals can be observed at 168 and 908 nm. The greater complexity of the surfactant F127 with respect to the ionic ones allows a certain degree of interaction, giving rise to aggregates with greater hydrodynamic diameters. The sizes determined by DLS are typically smaller than those observed by TEM, especially in the case of high aspect ratio materials such as MWCNTs or the non-covalently modified MWCNTs described in this work. The DLS technique determines the average speed at which particles move in the suspension [41]. The hydrodynamic size, as measured by DLS, is defined as the size of a hypothetical hard sphere that diffuses the same way as the measured particle. The hydrodynamic diameter, also known as the Stokes diameter, is the diameter of a sphere with the same translational diffusion coefficient as the particle being measured, assuming the presence of a hydration layer surrounding the particle. In any case, and regardless of the size of the species present, the goodness of fit and the data quality is evidenced by the abrupt drop in the correlation coefficient over time to values that are practically zero (Figure S2) [41]. Over and above, if the surfactant and the MWCNT are not subjected to a dry treatment with the ball mill, the correlation coefficient decrease is less pronounced and damped over time. That indicates the Brownian motion conditions are not preserved, and in fact, sedimentation of a proportion of the material can be seen by sight [40].

On the other hand, the ζ-potential values are consistent with the nature and charge of the surfactants that modify the surface of the MWCNTs (see Table 1): positive, negative, and around neutrality for CTAB, SDS, and F127, respectively. Contrary to some articles [42], particles without a net charge can remain dispersed as stable colloids

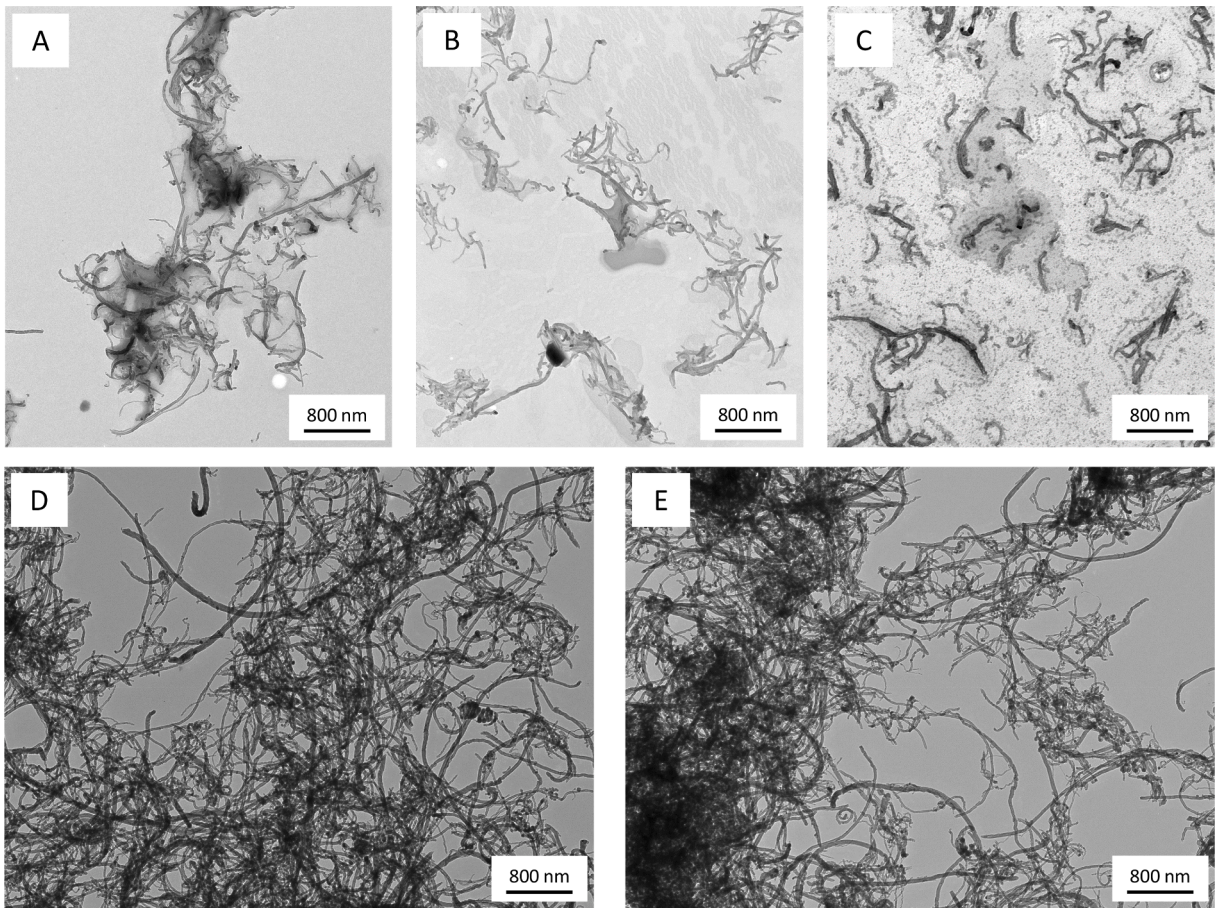

Fig. 3. TEM images of samples ground in the ball mill (A) MWCNT/CTAB, (B) MWCNT/SDS and (C) MWCNT/F127, (D) the commercial MWCNT and (E) the commercial MWCNT processed in the ball mill without surfactant.

due to the preservation of Brownian motion. The net charge is not the only factor involved in the stability of suspensions [43]. Steric hindrances and the interaction of the particle surface with the surrounding medium can minimise flocculation and sedimentation phenomena, even in particles with a net charge close to or equal to zero. In fact, finding particles with a size close to a micron and that present such good correlation curves in the DLS measurements implies their high stability, regardless of their surface charge.

The relationship between surfactants and MWCNTs is controversial and is not the focus of our study. However, it is worth noting that regardless of the type of organisation that occurs (whether it is MWCNT encapsulated in a cylindrical surfactant micelle, hemimicellar adsorption of surfactant molecules on the carbon nanotube surface, or random adsorption) [44,45], when we apply our mechanochemical protocol in the absence of solvents, the non-covalent interaction between the two components seems to be favoured (and also seems to be very homogeneous over the entire surface of the nanotube) based on their easy and rapid dispersion without requiring any additional post-treatment.

3.2. MWCNT-surfactant interaction

Once the fast dispersion and stability of the MWCNTs functionalised with surfactants have been shown, our interest is focused on demonstrating the preservation of the structure of carbonaceous materials. From a morphological point of view and at a structural level, the TEM images and the XRD data indicate that no alteration has occurred with respect to the starting material (see Supplementary information). However, some alterations could have been induced by the milling at the local level. Therefore, a sample that results from the exhaustive washing of the MWCNT functionalised with CTAB, which allows the elimination of the surfactant, was prepared and characterised. TEM images (Figure S3) and the XRD patterns of this washed sample and the commercial reagent are indistinguishable. Determination of the particle size of the MWCNTs has been carried out dryly by using a Malvern Mastersizer 2000 equipment (see Figure S4). A sharp peak is observed in both samples, which extends between 2 and 30–40 μm, with the commercial and washed samples having maximum values centred at 11 and 9 μm, respectively. The maximum signal value aligns with the specifications provided by the MWCNT supplier. The width of the signal and its extension up to a few tens of microns is likely associated with the presence of entangled MWCNT particles, as shown in the TEM images. The differences between the two curves are insignificant and could be explained by the fact that the sample of washed MWCNTs was subjected to a previous detangling process. No signals indicating the presence of significant populations of small carbon fragments were observed. Additionally, no significant differences were detected in the small size region (0.5–10 μm) between both samples, indicating that the ball mill treatment did not affect the average length of the MWCNTs. However, to analyse the possible alterations at the nanometric scale in more detail, a study was carried out using HRTEM (Fig. 5). The outer and inner diameter values estimated from the HRTEM images for the commercial MWCNTs (Fig. 5A; OD and ID in the ranges 32–34 nm and 7–9 nm, respectively) and the MWCNTs mechanochemically treated together with CTAB in the ball mill and later cleaned of surfactant (Fig. 5C; OD and ID in the ranges 35–36 nm and 8–9 nm, respectively) are very similar. These values are in good agreement with the specifications provided by the supplier. Additionally, both samples exhibit similar inter-spatial separations of MWCNTs graphene layers of about 0.35 nm

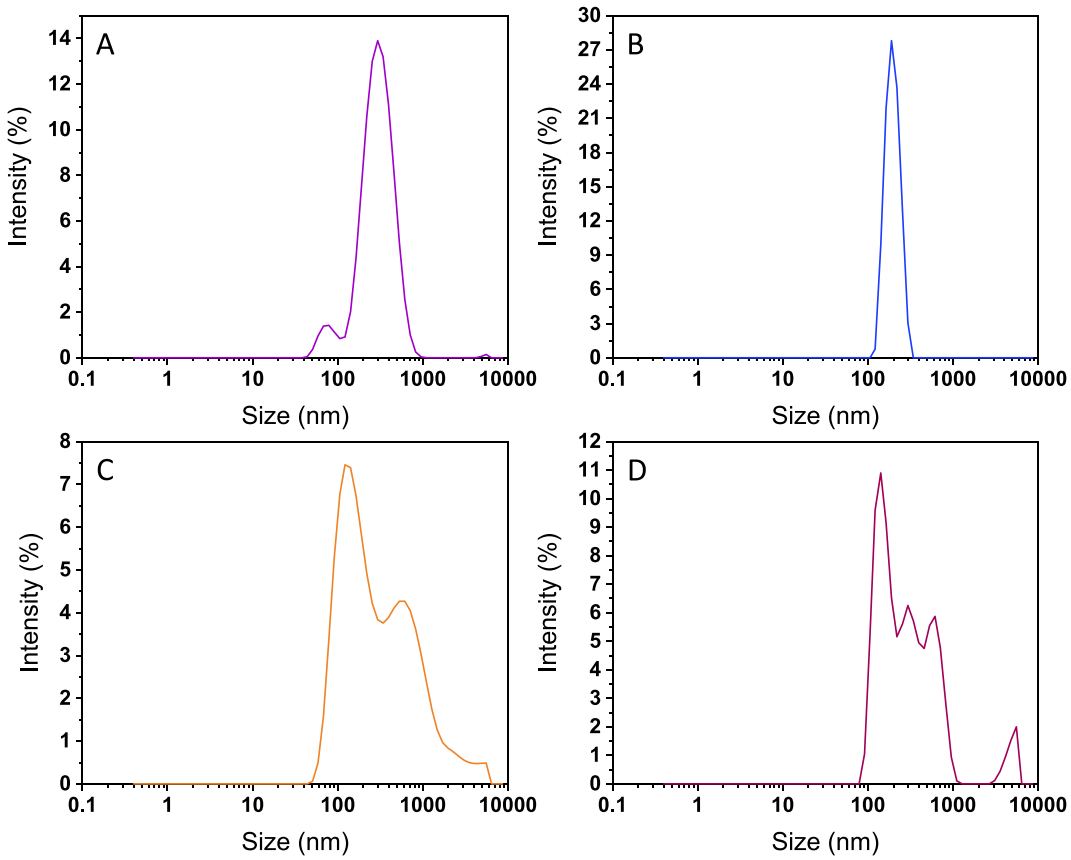

Fig. 4. DLS curves of dispersions of samples ground in the ball mill (A) MWCNT/CTAB, (B) MWCNT/SDS and (C) MWCNT/F127, and (D) the sample MWCNT/CTAB without the mechanochemical treatment.

Table 1
ζ-potential values of mixtures of MWCNT and surfactants processed in the ball mill and dispersed in aqueous medium.

Sample	ζ potential (mV)
MWCNT/CTAB	+39.9 (14.5)
MWCNT/SDS	−28.7 (3.5)
MWCNT/F-127	−0.992 (3.8)

(Fig. 5 B and D). The values of the two samples coincide and agree with the supplier's data, indicating that the mechanochemical treatment has not altered the nature of the MWCNTs.

To analyse whether any covalent functionalisation has occurred on the MWCNT, the IR spectra of the starting material, the material treated in the ball mill and that obtained by successive washings have been recorded. As seen in Fig. 6, there is no signal attributable to vibrations of organic groups or simply hydroxyl species. No appreciable bands are detected around 3400 cm^{-1} (which could correspond to stretching vibrations of isolated surface –OH and/or –OH residues in carboxyl groups and in adsorbed water). Then, the small bands observed in the 1750–1550 cm^{-1} range can only be attributed to C = C bonds in aromatic rings [46,47]. The absence of other significant signals allows us to rule out the presence of other groups, such as carboxylic acid, ketone or quinone. In short, the dominant signals detected must be associated with C = C bonds typical of non-altered MWCNTs. Therefore, the IR results show no covalent modification into the nanotube surface, but this result could be confirmed with the Raman spectroscopy. The Raman spectra in Figures 7 and S4 show the typical bands of MWCNT and the different surfactants employed.Fig. 7..

The strongest and most widely studied Raman bands for carbon nanotubes and their composites are the D band, G band, and 2D band (also named G' band) due to their rich information regarding the microstructure of carbon materials [48,49]. Carbon nanotubes can be functionalised through covalent and non-covalent means (π − π electrostatic interactions). In both cases, a defect is introduced on the surface of the nanotube, where covalent functionalisation leads to an alteration of the sp^2 hybridisation, while non-covalent functionalisation results in impurities in the form of a coating. These defects can be characterised using Raman spectroscopy [50]. Generally, the Raman spectra of functionalised carbon materials have significantly enhanced D bands, broadened G bands, and possibly a weakened or absent 2D band, resembling the spectra of amorphous carbon [51]. So, the ratio of the areas corresponding to the bands D and G (A_D/A_G) quickly indicates the degree of functionalisation [52]. Table 2 shows the ratio of the areas corresponding to the bands D and G extracted from the Raman spectra. Coating carbon nanotubes with different surfactants increases the number of defects (higher A_D/A_G ratio) compared with the pristine MWCNT. In addition, in the case of short-chain surfactants (CTAB and SDS), the introduced defects are smaller than in the Pluronic F-127 surfactant, which has a much larger carbon chain. The increase in the A_D/A_G ratio after treating the MWCNTs with surfactants in the ball mill indicates that they are inducing a defect on the surface of the carbon nanotube due to their coating (non-covalent). Furthermore, considering the position of the MWCNT bands in Fig. 6, a slight displacement of the peaks can be observed when the MWCNT is coated with the surfactants. This effect is consistent with a non-covalent functionalisation through weak interactions between the MWCNTs surface and the hydrophobic tails of the surfactant [53]. Therefore, with the Raman spectroscopy, TEM images, and XRD diffractogram, we can confirm that the MWCNT has been successfully functionalised non-covalently with different surfactants using the ball milling process.

The electrical conductivity and Seebeck coefficient of nanotubes are

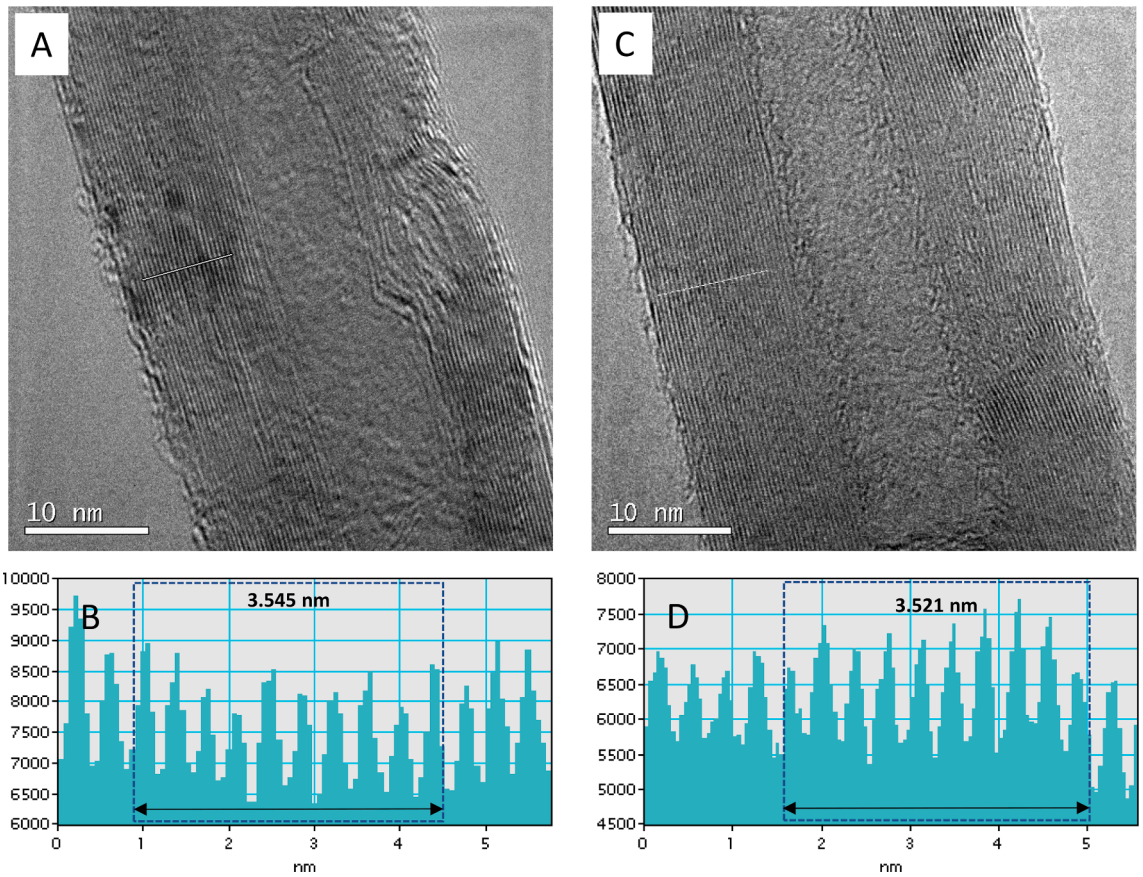

Fig. 5. Representative HRTEM images along with the corresponding line profiles of the interspatial MWCNTs graphene layer separation. (A) and (B) MWCNTs received from Nanoamor. (C) and (D) MWCNTs milled with the CTAB in the ball mill and later cleaned of surfactant.

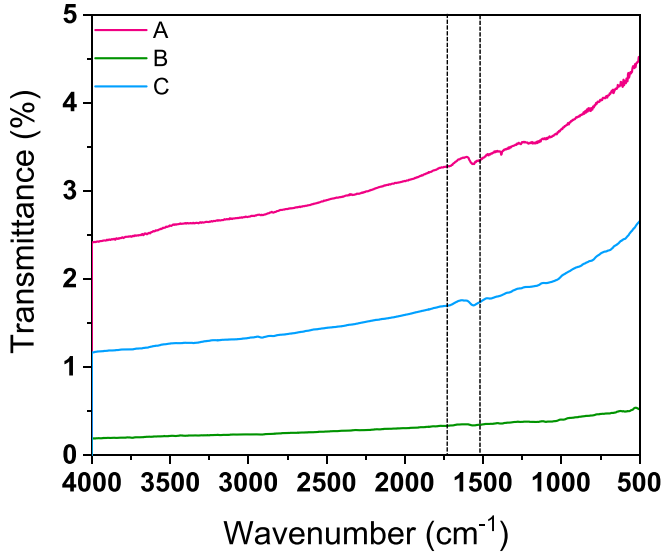

Fig. 6. FTIR spectra of the starting MWCNTs without milling (A), milled without surfactants (B) and the MWCNTs milled together with the CTAB in the ball mill and later cleaned of surfactant (C).

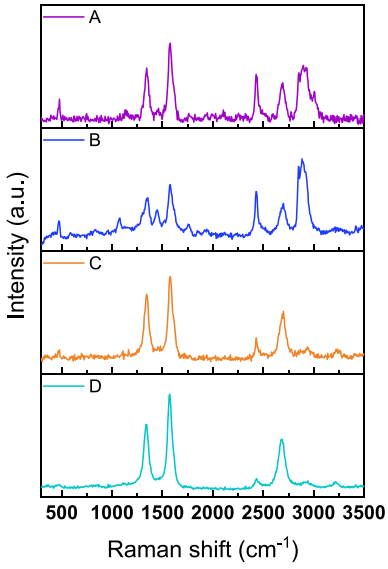

Fig. 7. Raman spectra of samples ground in the ball mill (A) MWCNT/CTAB, (B) MWCNT/SDS and (C) MWCNT/F127. (D) The commercial MWCNT.

closely related to their electronic structure [54]. Therefore, the introduction of covalent functionalisation in the structure of the carbon nanotube will produce an alteration of the sp^2 conjugation of the carbon, which will impair its electronic properties. In addition, the electrical conductivity of the carbon nanotube depends on its length [55]. Therefore, the measurement of electronic conductivity and the Seebeck coefficient will provide irrefutable proof of the integrity of carbon nanotubes after treatment with the ball mill and their functionalisation with surfactants. MWCNT pellets with a diameter of 1 cm and an average thickness of 0.5 mm were prepared. Fig. 8(a) shows the evolution of the electrical conductivity of carbon nanotubes after the different processes applied.

Table 2
Ratio of the areas corresponding to the bands D and G extracted from the Raman spectra.

Sample	A_D/A_G
MWCNT	0.54
MWCNT/CTAB	0.62
MWCNT/SDS	0.63
MWCNT/F-127	1.25

On the one hand, we observe that the electrical conductivity of the pristine MWCNT and the ground one (without surfactant) is practically the same. The slight increase observed is mainly because a pellet with a higher density can be achieved after treatment with the ball mill. On the other hand, when the MWCNTs are functionalised with the surfactant (CTAB), the electrical conductivity decreases because the surfactant electrically insulates the nanotube. Proof of this is that when the MWCNT@CTAB is washed with ethanol, we almost eliminate the CTAB and the electrical conductivity returns to its initial state. The fact that the electrical conductivity does not decrease after the treatment with the ball mill indicates that the length of the carbon nanotube is not being altered, in agreement with the TEM images. Fig. 8(b) shows the Seebeck coefficient of the carbon nanotubes after the different treatments. A Seebeck coefficient of around 20 μV K^{-1} is obtained in all cases, similar to the value obtained in other works [56–59]. Since the Seebeck coefficient only depends on the electronic structure, this result reinforces the conclusion that the functionalisation we are carrying out with the surfactants is non-covalent since they do not introduce defects in the sp^2 structure of the carbon nanotube. Therefore, the electrical conductivity and Seebeck coefficient measurements reinforce the results obtained by XRD, Raman and TEM images that the mechanochemical functionalisation with surfactants is non-covalent and does not break carbon nanotubes.

Based on the results, we can confirm that the method developed in this work may greatly interest the scientific community in preparing highly stable colloidal dispersions of MWCNTs with known concentration. These MWCNT dispersions can be utilised in numerous applications, especially in electronics (Schottky contacts [60], [biosensors [61], transistors [62], thermoelectrics [63]) and environmental sciences (metal sorption [64], removal of aromatic compounds and dyes [65,66]).

4. Conclusion

In this paper, we describe in detail a mechanochemical strategy combining surfactants with ball milling to produce non-covalently functionalised MWCNTs with high dispersibility in hydrophilic media. The key to this process is the treatment of MWCNTs and surfactants under dry conditions, aligned with the principles of green chemistry. That is an aspect that has not been addressed in the literature. This simple synthesis modification allows the highly dispersible carbonaceous material to be prepared in a single step in a few minutes without laborious post-treatment such as centrifugation or ultrasound. Furthermore, we achieved higher dispersion degrees (ca. 0.06 % (w/w)) than those described in the literature in hydrophilic solvents (usually in the 0.02–0.04 % (w/w) range) and, above all, with the full use of MWCNTs (100 % yield). All the MWCNTs introduced into the ball mill are eventually dispersed. All this without changing the nature of MWCNTs. The strategy is applicable to surfactants of different natures, including CTAB, SDS, and F127. The dispersibility values and preservation of colloidal conditions are similar for all three types of surfactants. Most likely, the methodology should be able to be extended to the use of other surfactants. As the surfactant type modifies, among other parameters, the external charge of the functionalised MWCNT, the choice of surfactant may depend on the final application, operating conditions, or post-synthesis stages if used for constructing more complex nanomaterials. Given the diversity of fields and applications involving MWCNTs, this method is of broad interest to the materials chemistry community. It is a highly reproducible and sustainable strategy and easy to replicate in which an expensive reagent such as MWCNTs is not wasted.

CRediT authorship contribution statement

M. Dolores Garrido: Conceptualization, Formal analysis, Investigation, Methodology, Writing – original draft, Validation. **José F. Serrano-Claumarchirant:** Formal analysis, Investigation, Methodology, Writing – original draft. **Sonia Murcia-Mascarós:** Investigation. **David Vie:** Investigation, Validation. **Francisco Pérez-Pla:** Investigation. **Jamal El Haskouri:** Investigation, Methodology, Validation. **José Vicente Ros-Lis:** Conceptualization, Funding acquisition, Visualization, Writing – original draft, Writing – review & editing, Methodology, Project administration, Supervision. **Pedro Amorós:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Visualization, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

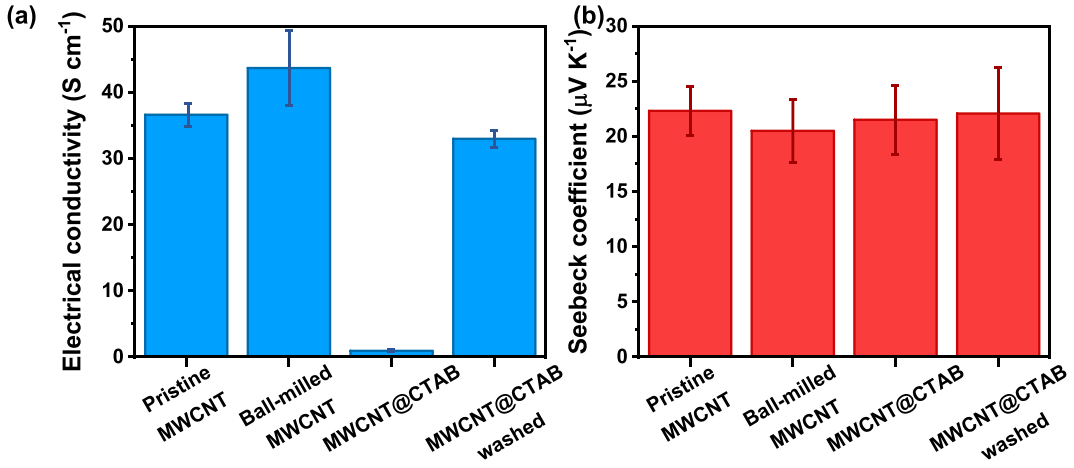

Fig. 8. Evolution of (a) electrical conductivity and (b) Seebeck coefficient of the carbon nanotubes at different stages of the procedure: pristine MWCNT, MWCNT after ball-milled process without surfactant, MWCNT@CTAB ball-milled, and MWCNT@CTAB ball-milled after washed.

Data availability

Data will be made available on request.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2024.124703.

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