Surfactant-mediated dispersions of carbon nano-onions in aqueous solution

Adalberto Camisasca and Silvia Giordani
School of Chemical Sciences, Dublin City University (DCU), Glasnevin, Dublin 9, Ireland
E-mail: silvia.giordani@dcu.ie

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Abstract
In this work, we investigate the ability of different surfactants to form homogeneous and stable dispersions of carbon nano-onions (CNOs) in water via non-covalent interactions. For our purposes, we select three ionic surfactants, namely the cationic hexadecyltrimethylammonium bromide (CTAB) and the two anionic deoxycholic acid sodium salt (DCAS) and sodium dodecylbenzenesulfonate (SDBS). We examine the dispersing efficacy at dispersing CNOs and long-term stability by UV–vis absorption spectroscopy, dynamic light scattering and zeta-potential. Among the three surfactants, the anionic surfactants show the best ability to create stable CNO dispersions, with SDBS exhibiting superior efficacy. Our non-covalent strategy provides a valuable approach to enhance the solubility features while preserving the unique properties of CNOs.

1. Introduction
Carbon nano-onions (CNOs) are attractive carbon nanomaterials (CNMs) that have aroused great scientific interest predominantly in the last decade, despite their discovery in 1992 [1]. Thanks to their appealing features, such as high surface area, ease of functionalization and biocompatibility, potential applications of CNOs include biomedicine [2] and electronics [3].

The main technical barrier that hindered, to some extent, the applications of CNOs relies on their hydrophobicity, which leads to the aggregation by intermolecular interactions. CNOs in their pristine form (p-CNOs) are, in fact, insoluble in aqueous media [4].

The development in recent years of efficient chemical approaches based on covalent and non-covalent functionalization of the CNO surface has helped to address this drawback, opening the way for their use in a vast range of applications [5, 6].

Covalent approaches rely on the introduction of polar groups onto the CNM surface to achieve homogeneous and stable dispersions. Several covalent functionalization strategies have been reported to increase CNO biocompatibility in vitro [7, 8] and in vivo [9, 10]. One drawback of covalent approaches is the modification of the regular sp²-hybridized carbon structure and the introduction of defects on the surface [11, 12]. Non-covalent functionalization is a convenient way to retain the native structure and intrinsic physiochemical properties of CNMs, while improving their solubility, as it relies on the adsorption of molecules onto the material surface through π−π, electrostatic and hydrophobic interactions [12−14].

Several non-covalent strategies have been reported so far for CNMs such as carbon nanotubes (CNTs) [12, 15] and graphene and its derivatives [16]. However, there are only a few papers on the non-covalent functionalization of CNOs [17−19].

Due to their commercial availability, low cost, and easy modification approaches, surfactants have a long and successful history as dispersing agents for CNMs such as CNTs [20−23]. In general, amphiphilic surfactants exhibit hydrophobic tail groups that interact with the hydrophobic graphitic surface of the CNMs, and hydrophilic head groups that, exposed to the aqueous environment, promote the material dispersion [24, 25].
In 2017, Plonska-Brzezinska et al reported the ability of the cationic hexadecyltrimethylammonium bromide (CTAB), the anionic sodium dodecyl sulfate (SDS) and sodium dodecylbenzenesulfonate (SDBS) and the non-ionic 4-(1,1,3,3-tetramethybutyl)-phenyl-polyethylene glycol (Triton X-100) and polyethylene glycol sorbitan monolaurate (Tween 20) surfactant molecules to stabilize p-CNOs in aqueous solutions. In particular, the formation of stable CNO solutions was achieved for surfactant concentrations below 1 mg ml\(^{-1}\) [19].

Herein, we report the non-covalent surface modification of p-CNOs with three different commercially available ionic surfactants, the cationic CTAB and the two anionic deoxycholic acid sodium salt (DCAS) and SDBS. Two CNO:surfactant mass ratios (i.e., 2:1 and 5:1) have been examined, and the dispersing abilities and long-term stability of the three ionic surfactants have been investigated and characterized by UV–vis absorbance spectroscopy, DLS and zeta-potential.

2. Experimental

2.1. Synthesis of pristine carbon nano-onions

Pristine carbon nano-onions (p-CNOs) have been synthesized by thermal annealing of detonation nanodiamonds following a previously reported procedure [8, 26].

2.2. Non-covalent functionalization of p-CNOs with surfactants

The three surfactants were purchased from Fisher Scientific and used as received. p-CNOs were dispersed in deionized water and sonicated for 10 min to obtain a 1 mg ml\(^{-1}\) dispersion. Then, the right amount of surfactant was added, and the suspension was sonicated for 30 min to yield CNO:surfactants mass ratios of 2:1 and 5:1. The same experimental procedure was employed for the functionalization with the three surfactants.

2.3. Material characterization

2.3.1. UV–vis absorption spectroscopy

UV–vis absorption spectra were acquired on a Shimadzu UV-1800 spectrophotometer using standard quartz cuvettes with a 1 cm path-length. The different samples at 1 mg ml\(^{-1}\) as CNO concentration obtained from the functionalization procedure were initially diluted to 100 μg ml\(^{-1}\) and then, after sonicing for 15 min at 37 kHz, further diluted to 5, 10, 20 and 50 μg ml\(^{-1}\) for the analyses. Depending on the CNO:surfactants mass ratios, the as-prepared CNO concentrations (1000, 100, 50, 20, 10 and 5 μg ml\(^{-1}\)) correspond to different surfactant concentrations. In particular, for the 2:1 mass ratio, those concentrations correspond to a surfactant concentration of 500, 50, 25, 10, 5 and 2.5 μg ml\(^{-1}\), while, for the 5:1 mass ratio, to a surfactant concentration of 200, 20, 10, 4, 2 and 1 μg ml\(^{-1}\).

2.3.2. Dynamic light scattering and zeta-potential

Dynamic light scattering (DLS) analyses were carried out using a Malvern Zen 3600 Zetasizer in backscattering (173°) mode and with automatic selection of the optimal detector position. The same instrument was used for the zeta-potential analyses using Malvern disposable cuvettes. The analyses have been performed in deionized water at neutral pH conditions.

3. Results and discussion

Nanodiamond-derived CNOs typically display a primary particle size ranging between 5 and 8 nm [8]; however, when in solution, the particles rearrange to form large aggregates as a consequence of the marked hydrophobicity driven by intermolecular interactions between the nanoparticles [4].

In particular, as p-CNOs are totally insoluble in aqueous media, a high degree of agglomeration is observed with the presence of micro-scaled aggregates even after prolonged sonication processes, making impossible their proper dispersion in aqueous solutions and thus their use in water-based applications. In efforts to make p-CNOs soluble in aqueous medium, and thus attracting for several applications, we investigated the dispersing capability of three different commercially available surfactants and compared their ability to promote the CNO dispersion by preparing two different CNO:surfactant mass ratios, namely 2:1 and 5:1. It has to be noted that, without the aid of the surfactants, it is impossible to disperse CNOs in water. In general, the efficacy of the dispersion process mediated by the surfactants is due to the material-surfactant interactions and the surfactant structural features such as type and charge of polar groups as well as the alkyl chain length [21]. For this reason, we selected three ionic surfactants with different chemical structures (figure 1).

Hexadecyltrimethylammonium bromide (CTAB) is a cationic surfactant showing an alkyl chain as a hydrophobic tail and a positive quaternary ammonium head as the hydrophilic region (figure 1(A)). The CTAB adsorption is expected to occur by hydrophobic interactions between its extended alkyl tails and the CNO
surface, while the CNO dispersion to be promoted by the positive hydrophilic groups exposed to the aqueous environment that prevents CNO aggregation due to electrostatic repulsions between the polar heads [27].

Deoxycholic acid sodium salt (DCAS) is an anionic surfactant. Being part of the family of bile acid salts, it is composed of a steroid nucleus consisting of three six-membered and one five-membered hydrocarbon rings and a short hydrocarbon tail bearing COO− group (figure 1(B)). The adsorption of DCAS molecules over the CNO backbone is driven by hydrophobic interactions between the steroid backbones of the surfactant and the carbon network [25].

Sodium dodecylbenzenesulfonate (SDBS) is an anionic surfactant with a structure composed of a hydrophobic alkyl-benzene tail and a hydrophilic sulfonate head (figure 1(C)). Its adsorption is promoted by hydrophobic interactions between CNOs and the aliphatic tails [28].

The dispersing abilities of the different surfactants have been investigated by UV–vis absorption spectroscopy. The absorption spectra of CNO:CTAB and CNO:DCAS derivatives for the two tested mass ratios at different concentrations are shown in figures S2(A) and (C) and S3(A) and (C), respectively. Compared to the UV–vis spectra of CTAB and DCAS aqueous solutions (figures S1(A) and (B)) is available online at stacks.iop.org/NANOX/1/010018/mmedia), which exhibit no distinctive absorption features, the surfactant-dispersed CNOs show a prominent peak located at 263 nm, attributed to the π → π∗ transitions of the C–C bonds, and exhibit absorption in the entire wavelength region for both ratios. This is assigned to the absorption of the CNOs, thus confirming the ability of both surfactants to disperse the carbon material.

The UV–vis absorption spectra of the CNO:SDBS derivatives, shown in figures S4(A) and (C), are characterized by three absorption peaks located below 200 nm, at around 225 nm, and at 263 nm, respectively. Since SDBS does not exhibit absorption in the entire wavelength range (figure S1(C)), the absorption above 300 nm can be assigned to CNOs, thus proving the success of the non-covalent functionalization approach.

In order to compare the dispersing abilities of the different surfactants, we plotted the absorbance values for the different derivatives at a concentration of 100 μg ml⁻¹ calculated at a wavelength of 400 nm. This particular wavelength has been chosen as none of the surfactants show distinctive absorbance at this point. From the analysis of figure S5, we can point out that the dispersion capability is dependent on the CNO:surfactant mass ratio. In general, at a 5:1 mass ratio, all the CNO derivatives exhibit higher absorbance values compared to that at 2:1 for all the surfactants tested, thus resulting in better dispersion of the CNOs in the aqueous surfactant solutions. In particular, the results show that SDBS has the best ability to promote the CNO solubilization at this mass ratio, while similar results are observed for CTAB and DCAS. Our results strongly suggest that the optimal CNO:surfactant mass ratio, in terms of dispersion efficiency, is 5:1. Nevertheless, it should be noted that all the surfactants form homogeneous CNO dispersions at a 2:1 mass ratio.

In order to calculate the surfactant effectiveness to create stable CNO dispersions, sedimentation experiments were performed at a 100 μg ml⁻¹ as CNO concentration. We exploited the Lambert–Beer law to obtain the extinction coefficient for all the derivatives (figures S2(B) and (D), S3(B) and (D), and S4(B) and (D)) and used these values for the determination of the CNO concentrations.

Figures 2(A) and (D) show the UV–vis absorption spectra of CNO:CTAB 2:1 and CNO:CTAB 5:1 at different times (immediately after sonication, and after one, two and six weeks) in deionized water, starting from a CNO concentration of 100 μg ml⁻¹. The results show that, although CTAB is effective at dispersing CNOs, a quite

![Figure 1. Chemical structure of (A) CTAB, (B) DCAS, and (C) SDBS.](image-url)
rapid decrease in the concentration is observed with respect to time due to a re-aggregation process occurring right after sonication. In particular, after six weeks, only 53% and 37% of the material is still in solution for 2:1 and 5:1 mass ratios, respectively (table S1). This trend is further confirmed by the analysis of the solutions at different time points (figure 3), revealing the fast settlement of the CNOs overtime.

A different behavior is instead observed for the anionic surfactants. The analysis of figures 4(A) and 4(D) and 6(A) and (D) reveals that CNOs dispersed in DCAS and SDBS are much more stable than those dispersed in CTAB. As depicted from tables S2 and S3, the CNO dispersions retained more than 75% of the initial material concentrations after six weeks. In particular, DCAS showed the highest stability, with approximately 87% and 85% of the material still dispersed at 2:1 and 5:1 mass ratios, respectively. This is contrasted by approximately 83% and 76% shown by SDBS at the same ratios, respectively. Further evidence of the superior CNO dispersion stabilization abilities of both surfactants is provided by the analysis of the solutions (figures 5 and 7).

The sedimentation analyses showed that the anionic DCAS and SDBS ensured long-term stability to the CNO aqueous dispersions with minimal absorbance decrease after at least six weeks, while at the same time, the lowest dispersibility was observed for cationic CTAB.

Further information about the dispersibility and stability of the CNO derivatives have been obtained by dynamic light scattering (DLS) and zeta-potential analyses. DLS measurements were employed to determine the hydrodynamic radius of the different CNO aqueous dispersions. DLS spectra of CNOs stabilized by CTAB, DCAS, and SDBS at the two investigated mass ratios for a concentration of 100 μg ml⁻¹ are shown in panels B & E of figures 2, 4 and 6. As depicted in table 1, CNO:CTAB 2:1 and 5:1 reveal a hydrodynamic diameter equal to 203.3 and 183.1 nm, respectively, confirming the good dispersing abilities of CTAB at dispersing CNOs, in contrast to the marked water insolubility of p-CNOs. After one week, a similar decrease in the size is observed for both mass ratios, which is assigned to the sedimentation of large aggregates. After two weeks, both ratios display higher size values, suggesting an aggregation process occurring in the samples, in line with the UV–vis
Figure 4. UV–vis absorption spectra of (A) CNO:DCAS 2:1 and (D) CNO:DCAS 5:1 at different times (after sonication and after one, two and six weeks) in deionized water starting from a concentration of 100 μg ml⁻¹. DLS and zeta-potential analyses of CNO:DCAS 2:1 (B) and (C) and CNO:DCAS 5:1 (E) and (F) at different times (after sonication and after one, two and six weeks) in deionized water at a concentration of 100 μg ml⁻¹.

Figure 5. Pictures of (A) CNO:DCAS 2:1 and (B) CNO:DCAS 5:1 solutions at 100 μg ml⁻¹ in deionized water at different times: after sonication and after one, two and six weeks.

Figure 6. UV–vis absorption spectra of (A) CNO:SDBS 2:1 and (D) CNO:SDBS 5:1 at different times (after sonication and after one, two and six weeks) in deionized water starting from a concentration of 100 μg ml⁻¹. DLS and zeta-potential analyses of CNO:SDBS 2:1 (B) and (C) and CNO:SDBS 5:1 (E) and (F) at different times (after sonication and after one, two and six weeks) in deionized water at a concentration of 100 μg ml⁻¹.
spectroscopy results. In particular, after six weeks, the instrument was not able to provide any DLS spectra due to the high CNO aggregation in the samples, a consequence of the desorption of the surfactant molecules.

In contrast, p-CNOs dispersed by DCAS and SDBS show high stability over time (Tables 2 and 3), in perfect agreement with what observed from the sedimentation analyses. In particular, at both tested mass ratios, the CNOs were well-stabilized by the two surfactants, showing average size values in the range between 140 and 200 nm, without any significant variations over six weeks of analyses as compared to those shown by CTAB.

Zeta-potential analyses were carried out to determine the CNO surface charge in the surfactant dispersions, thus providing information about their stability. In fact, particles showing zeta-potential values higher than $|30|$ mV are generally stable as the repulsion forces hinder the material aggregation [19, 29]. Cationic and anionic surfactants are expected to confer opposite zeta-potential values to the stabilized materials as a consequence of their different surface charge [29, 30]. In particular, the CTAB quaternary ammonium heads and the COO$^-$ and sulfonate heads of DCAS and SDBS are presumed to impart, respectively, positive and negative charge to the CNO surface, preventing their aggregation.
Zeta-potential spectra of the different CNO water dispersions at a concentration of 100 μg ml⁻¹ are shown in panels C & F of figures 2, 4 and 6, while the corresponding values are reported in tables 1, 2 and 3. For the CNO:CTAB systems, both mass ratios exhibit positive zeta-potential values (+18.8 ± 5 and +16.7 ± 4 mV for 2:1 and 5:1, respectively), as expected from the positive charge of the surfactant head groups. However, a significant difference is observed in the zeta-potential values after one week. For the 5:1 derivatives, a more positive value is observed (i.e. +28.2 ± 4 mV), suggesting higher stability of the system. Conversely, a negative value is observed for the 2:1 mass ratio (i.e. −22.8 ± 4 mV), which can be ascribed to the lower stability of the CNO:surfactant system due to the detachment of CTAB from the CNO surface. In line with the UV–vis spectroscopy and DLS results, a reduced stability is observed over time for both ratios as a consequence of the high CNO aggregation in the samples, making impossible the zeta-potential evaluation at the six weeks time point.

In contrast, the anionic surfactant CNO dispersions are negatively charged as a consequence of the negative charged heads of DCAS and SDBS and display excellent stability overtime with zeta-potential values ranging between −45 and −30 mV. In particular, for CNO-containing DCAS dispersions, values equal to −39.3 ± 7 and −35.2 ± 6 mV are observed at the 2:1 and 5:1 mass ratios, while p-CNOs stabilized by SDBS exhibit values of −44.6 ± 6 and −37.1 ± 6 mV, respectively. The small variations of the zeta-potential values overtime (table 2 and table 3) well account for the enhanced water dispersability and stability imparted by the anionic surfactants to that shown by the cationic CTAB.

As discussed above, as CNOs are insoluble in aqueous solutions, homogeneous and stable aqueous dispersion of p-CNOs cannot be achieved, thus making impossible their use in water-based applications. Our results show that the proposed non-covalent modification of the CNO surface is effective to disperse p-CNOs in aqueous solutions. In particular, all the surfactants molecules are capable of enhancing the CNO dispersing features at both the mass ratios investigated, in agreement with what previously shown for CNOs dispersed by CTAB and SDBS for surfactant concentrations below 1 mg ml⁻¹ [19]. In addition, compared to what reported by Plonska-Brzezinska, our CNO dispersions exhibit lower average sizes of the aggregates, as calculated from DLS analyses, suggesting that, at the investigated mass ratios, CTAB and SDBS are capable of dispersing CNOs to a greater extent. Conversely, while similar zeta-potential values are observed for SDBS-stabilized CNOs, CNOs dispersed in CTAB display lower values, suggesting that lower surfactant concentrations allow for the formation of more stable CNO dispersions [19].

The differences in the dispersing abilities and stability of the tested surfactants can be ascribed, in the first instance, to their different chemical structure and ionic head groups. In general, the surfactant molecules promote the material dispersion placing their hydrophilic head groups towards the aqueous phase, thus reducing the material/water interfacial tension. The dispersing effectiveness of a surfactant is thus related to how strong it adsorbs onto the material surface [22, 31].

As confirmed by UV–vis spectroscopy, DLS and zeta-potential analyses, the solubilization and stabilizing effect is stronger for the anionic surfactants than that achieved by the cationic ones.

In particular, in the case of CTAB, the good CNO dispersion achieved at the beginning of the process is due to the strong absorption of the long hydrocarbon tails over the CNO surface by hydrophobic interactions [27]. However, these interactions seem to be insufficient for retaining the surfactant adsorbed onto the graphitic surface, as shown by the poor stability overtime of the CNO:CTAB systems, leading to a decreased aqueous affinity and thus to the re-aggregation and precipitation of the nanoparticles.

On the other hand, our results show a superior dispersing capability and excellent stability of the colloidal CNO dispersions provided by DCAS and SDBS, with the latter exhibiting slightly better performance. As it has been suggested that anionic surfactants would adsorb to negatively charged surfaces more strongly than cationic ones [29], this behavior can be assigned to the stronger hydrophobic interactions established between the CNO surface and the DCAS steroid backbone [25] or the SDBS alkyl chain tails [28], which lead to a higher adsorption and thus higher CNO surface coverage of the negatively charged surfactants. In addition, the polar head groups of the different surfactants play an important role in the water dispersion process. In particular, the DCAS − COO⁻ and the SDBS − SO₃⁻ groups have better solvation properties than the CTAB − N(CH₃)₃⁺ groups because of the spatial restriction of the methyl groups [32]. Therefore, the ability to bound more water molecules accounts for the better performance of the anionic surfactants.

Furthermore, the slightly better dispersing abilities displayed by SDBS can be attributed to the presence of the benzene ring in the molecule, that has been reported to be responsible for its higher dispersing efficiency due to the formation of π−π interactions with graphicitic surfaces [20, 28]. However, considering that the aromatic ring is at the hydrophilic end of the molecule and the steric hindrance caused by the sulfonate groups [33], the formation of these kind of interactions are quite unlikely. In particular, given the different chemical structure of DCAS and SDBS, it is hard to assign, and thus to explain with absolute certainty, the shown superior dispersing ability of the latter to the benzene ring factor without further investigations.
Apart from all, DCAS and SDBS have shown great premises at dispersing p-CNOs in aqueous solutions, making them essential for a future water-based application of CNOs.

4. Conclusions

Carbon nano-onions (CNOs) are an attractive carbon nanomaterial with interesting physico-chemical properties that make them an excellent candidate for several applications. However, the marked tendency of pristine CNOs (p-CNOs) to form aggregates in aqueous solutions requires appropriate surface chemical functionalization. Non-covalent modification with surfactant molecules has shown to be a viable strategy in enhancing the water solubility of different carbon nanomaterials, such as carbon nanotubes.

In this work, we have investigated the ability of three different commercially available ionic surfactants to disperse CNOs in aqueous solutions. All the surfactants tested were able to promote the CNO dispersion in water, with the 5:1 mass ratio showing the best results in terms of dispersibility. However, only SDBS and DCAS conferred long-term stability to the CNO constructs, as confirmed by UV–vis, DLS and zeta-potential analyses over a period of six weeks.

The different dispersing behavior has been ascribed to the different charge of the head groups as well as the chemical structure of the surfactants. In particular, our results show that the negatively charged head groups have superior ability to impart dispersibility and long-term stability in aqueous solutions to CNOs.

Our results show that the non-covalent functionalization of p-CNOs with surfactants can be an effective way to enhance the material solubility in aqueous media while retaining their native physico-chemical properties. This may pave the way for the possible use of CNOs in new and unexplored applications, such as in biomedicine, where its poor processability in the pristine form is a major challenge.

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ORCID iDs

Adalberto Camisasca @ https://orcid.org/0000-0002-0185-9656
Silvia Giordani @ https://orcid.org/0000-0002-9212-5067

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