



New metal-free nanolubricants based on carbon-dots with outstanding antiwear performance



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ABSTRACT

Nanoparticles have already demonstrated a good performance in improving the wear and/or coefficient of friction when used as nanolubricants. Nevertheless, they show two main drawbacks: most of them are metal-based and, therefore, eco-unfriendly, and they are mostly hydrophilic and, consequently, unstable in organic media, which finally drives to aggregation/sedimentation and the loss of the good properties.

In this work, we carry out the synthesis of carbon-based nanoparticles for additives in lubricants from two different approaches: either using ionic liquids as carbon source, or using glutathione as carbon source and decorating the so-obtained carbon dots with the big organic cations of the ionic liquid. The final materials (diameters between 2.2 and 3.5 nm) were characterized by TEM, FTIR, XPS, and luminescent methodologies, finding long-term stability of the suspensions in organic media (≥ 15 days). Carbon dots obtained directly from the ionic liquids, in particular from methyltriethylammonium chloride (MTOACDs) have demonstrated to be the best candidate as additive in different base oils (0.1%, w/v) and lubrication regimes, reducing the coefficient of friction about 30% and wear scar in more than 60% in the most extreme of the tested conditions (120 N). Additionally, nanolubricants are metal-free and therefore, more eco-friendly than classic additives.

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Introduction

Nanotechnology can be defined as the application of the science and engineering to practical use in the nanoscale. Since years, it is known that the properties of the matter are very different depending on the scale: bulk material or nanostructures. In fact, the development of nanotechnology has resulted in interesting applications in many different scientific fields, such as chemiluminescent enhancers in bioassays [1], imaging [2], diagnosis [3], medicine [4] or tribology [5] among others.

Although the excellent tribological performance of nanomaterials has already been well established [5], their extensive use as nanolubricants is hindered due to the instability of hydrophilic nanoparticles (NPs) in hydrophobic media such as base lubricant oils. NPs tend to form aggregates by irreversible clustering of individual NPs, yielding bigger structures which may lose their nano-size properties [6] or, even, undergoing

sedimentation. Such tendency is mainly driven by the surface chemistry, the nature of the solvent and/or the concentration of NPs [7,8]. A promising alternative to prevent the aggregation and/or sedimentation behaviour is by acting on the surface of the nanoparticles so as to improve their affinity for the solvent, as result of which inter-particle interaction probabilities are minimized [6]. The chemical modification of nanoparticle surface becomes, therefore, of paramount importance in the lubrication field. Carbon nanodots (CDs) are carbon-based nanostructures easily synthesized from almost any carbon source, including chemical reagents [9], biomolecules [10] or even foodstuff [11]. The versatility of the carbon source allows obtaining CDs with surface functional groups amenable for a further derivatization, being so an excellent option for lubrication purposes. On the other hand, ionic liquids (ILs) are also considered as promising additives for lubrication [12–14] due to their unique characteristics such as non-flammability, negligible volatility, controlled miscibility with organic compounds as well as high chemical and thermal stability [15–17].

In the last decade, the use of carbon structures for the improvement of the tribological properties of lubricants has

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evolved from the design of carbon microspheres such as ball bearings [18] to the nanostructures, for example, carbon quantum dots and graphene oxide dispersed in polyethylene glycol (PEG) [19] or water-based lubricants [20] with remarkable performance. Furthermore, strategies have been developed to obtain synthesis through the synergy between carbon nanostructures and ionic liquids such as the multi-walled carbon nanotubes modified with ionic liquids as an additive in base lubricant L-B104 (1-methyl-3-butylimidazolium tetrafluoroborate) [21] or ionic liquid capped carbon dots dispersed in water-based lubricants [22–24]. In these works, water and/or water based solutions, or the ionic liquid itself, were used as lubricants to evaluate the tribological performance of CDs as additives. The field of metal-free carbon dots as additives in oil-base lubricants is in its infancy.

In this work, taking into account the properties of both CDs and ILs, we describe the synthesis and characterization of new hybrid CDs prepared using citric acid and different ILs for using them as oil lubricant additives. The stability of the CD-base oils (polyalphaolefins, PAO) suspensions were studied and their tribological performance (wear and friction coefficient) was evaluated. Besides, for the sake of comparison, hydrophilic CDs were also synthesized from glutathione (GSH) [10] and their surface modified with ILs, forming ionic pairs between the GSH-CD and the long-chain ILs cations, rendering singular nanostructures that hold the unique properties of both CDs and ILs. The different surface chemistry of the synthesized CDs was a key parameter to prepare stable base oil suspensions and to use them as lubricant additives for reduction of wear and friction coefficient.

Experimental

Reagents

Citric acid monohydrate 99%, L-glutathione > 98% (GSH), methyltriethylammonium chloride > 97% (MTOAC), tributylmethylammonium chloride > 98% (TBMAC), 1-methyl-3-octyl-imidazolium chloride (MOIC), 1-hexyl-3-methyl-imidazolium chloride (HMIC) and dialysis membranes Pur-A-Lyzer Mega 1000 dialysis kit were purchased from Sigma–Aldrich; NaOH 98% were acquired from AlfaAesar; toluene and ethanol absolute were bought to VWR.

Synthesis of hybrid CDs from citric acid and ionic liquids

Citric acid-ionic-liquid carbon dots (ILCDs) were synthesized following a solvothermal carbonization method, according to the following procedure: 1.00 g citric acid and 0.50 g ionic liquid were weighted into an open Teflon beaker and 10 mL of an azeotropic mixture of ethanol–water (96%) was added. The mixture was placed in an ultrasonic bath at room temperature for 5 min in order to homogenize the mixture. Afterwards, the solution was heated into an oven at 180 °C for 90 min, adding 1 mL of the azeotropic mixture ethanol–water every 30 min (two times). Finally, the viscous brown liquid obtained was let to cool down to room temperature in a desiccator. The obtained ILCDs were labelled according to the IL used as follows: HMICDs (from HMIC), MOICDs (from MOIC), TBMACDs (from TBMAC) and MTOACDs (from MTOAC).

The final product was dispersed into 15 mL absolute ethanol using an ultrasound bath and dialyzed for 12 h against ethanol; following, most of the ethanol was removed in a rotatory evaporator. The residues were poured into a 5 mL flask and the remaining solvent was removed at room temperature under vacuum conditions. The final material was kept in a desiccator until further use.

Synthesis of IL surface-modified glutathione-based carbon nanodots (IL-GSHCDs)

Carbon nanoparticles obtained from glutathione (GSHCDs)

The GSHCDs were hydrothermally synthesized using the methodology proposed by Díaz-Faes López et al. [10] with slight modifications according to the following procedure: 2 g of citric acid plus 1 g glutathione were poured into a porcelain crucible and dissolved into 10 mL water using an ultrasonic bath for 5 min; then, it was placed into an oven at 180 °C for 150 min. 1 mL water was added to the mixture every 30 min (four times) in order to keep a minimum volume of solvent and avoid the material to scorch. The crucible was carefully transferred from the oven to a desiccator and let there to cool to room temperature. The final product was a viscous brownish liquid which was dispersed into 15 mL water with the help of an ultrasonic bath and the suspension was then dialyzed for 24 h using a high performance dialysis tube (capacity 3–20 mL, MWCO 1 kDa) against water. Once the process was completed, most water was removed from the GSHCDs in a rotatory evaporator and the final residue was then lyophilized, yielding an orange-brownish solid, which was kept in desiccator/fridge until further use.

Surface functionalization of GSHCDs with ILs

The surface functionalization was carried out via an active liquid–liquid extraction (toluene–water) of the GSHCDs as follows: 0.2 g of GSHCDs were dissolved into 30 mL water, and the pH was then raised to 9–10 using NaOH 0.1 M. Simultaneously, 0.12 g (~0.3 mmol) of the corresponding IL were dissolved into 30 mL toluene. Both solutions were then mixed and vigorously shaken for 72 h in a separation funnel. After that, the mixture was let to separate and the organic layer was washed twice with 30 mL of NaOH (pH 9–10). The toluene was then removed in a rotatory evaporator until dryness, yielding a solid residue of IL-GSHCDs ion pairs, which was kept in the fridge/desiccator until further use.

Stability of carbon dots in aqueous and hydrophobic media.

Different CD suspensions in the range 0.01–0.35% (w/v) were prepared by dispersing the proper amount of solid CDs in 30 mL solvent (toluene, ethanol or water) and sonicated it for 10 min. On the other hand, 0.1–0.25% (w/v) CDs suspensions were dispersed in 10 mL of base oil BO68 and sonicated until a homogenous dispersion was obtained. In this work, we assume as 'stable nanoparticle dispersion' or 'stable nanoparticle suspension' those dispersions/suspensions which remained without perceptible aggregation or sedimentation to the naked-eye after 15 days rest.

Instrumentation

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was carried out in a Varian 670-IR spectrometer with a Golden Gate ATR device. The spectra were taken from 600 to 4000 cm^{-1} with 4 cm^{-1} resolution at 2000 cm^{-1} as the average of 16 scans. Background was taken without any sample in the ATR crystal and the sample was measured pressing the powder against the crystal with an anvil.

UV–vis characterization was performed in a Cary 60 UV–vis spectrometer, and the photoluminescence spectra were taken in a Varian Cary Eclipse spectrofluorimeter with a 1 × 1 × 4 cm quartz-cell. Time-resolved photoluminescence measurements were carried out with a FLSP 920 spectrofluorimeter from Edinburgh Instruments. Absolute quantum yields (Φ_{abs}) were obtained by detecting all sample fluorescence through the use of an integrating sphere in FS5 Spectrofluorometer (from Edinburgh Instruments) and using Fluoracle software.

The morphological characterization, as well as the size determination of CDs were performed by HRTEM, using a JEOL JEM-2100F, 200 kV. The average diameter and the standard deviation were determined from the digitalized images with the software ImageJ Tool, taking into consideration at least 150 observations.

The surface of the final materials was analyzed with X-Ray photoelectron spectroscopy (XPS). These spectra were taken using a Phoibos 100 MCD5 hemispherical electron analyser from SPECS and X-Ray from Mg K α , (1253.6 eV) in a vacuum chamber with pressure below 5×10^{-9} mbar. Data acquisition was carried out using 90 eV pass-energy and 1 eV energy step for survey spectra and 30 eV pass-energy and 0.1 eV energy step for high resolution spectra.

Wear and friction tests were performed with a Bruker UMT3 tribometer under normal loads of 60 and 120 N. Worn surfaces were analyzed with confocal and interferometric microscopy with a DCM3D Leica microscope.

Results and discussion

Most of the carbon dots suspensions reported in the literature are stable mainly in aqueous media [25,26] due to an intrinsic surface functionalization with Lewis acid-base groups present in the starting reagents. As the aim of the work is the use of CDs as additives in hydrophobic media (lubricant base oils, organic solvents), two strategies using citric acid as the carbon source were followed (Scheme 1): (A) the one-step hydrothermal method, in the presence of ionic liquids with long alkyl chains which provided the hybrid CDs with a hydrophobic character (butyl, hexyl, octyl); and (B) the two-steps ion-pair method, taking advantage of the surface functional groups ($-\text{COOH}$, $-\text{NH}_2$, $-\text{SH}$) present in GSHCDs to form extractable ion-pairs with ILs. In both cases, the CDs were synthesized via thermal oxidation using an ad hoc solvent, which could solubilize all the reagents. Such a solvent was ethanol-water (96%) in the one-step methodology and water in the

two-steps case. Also, in both approaches two-thirds of the initial reagents mass was citric acid, acting as the main carbon source.

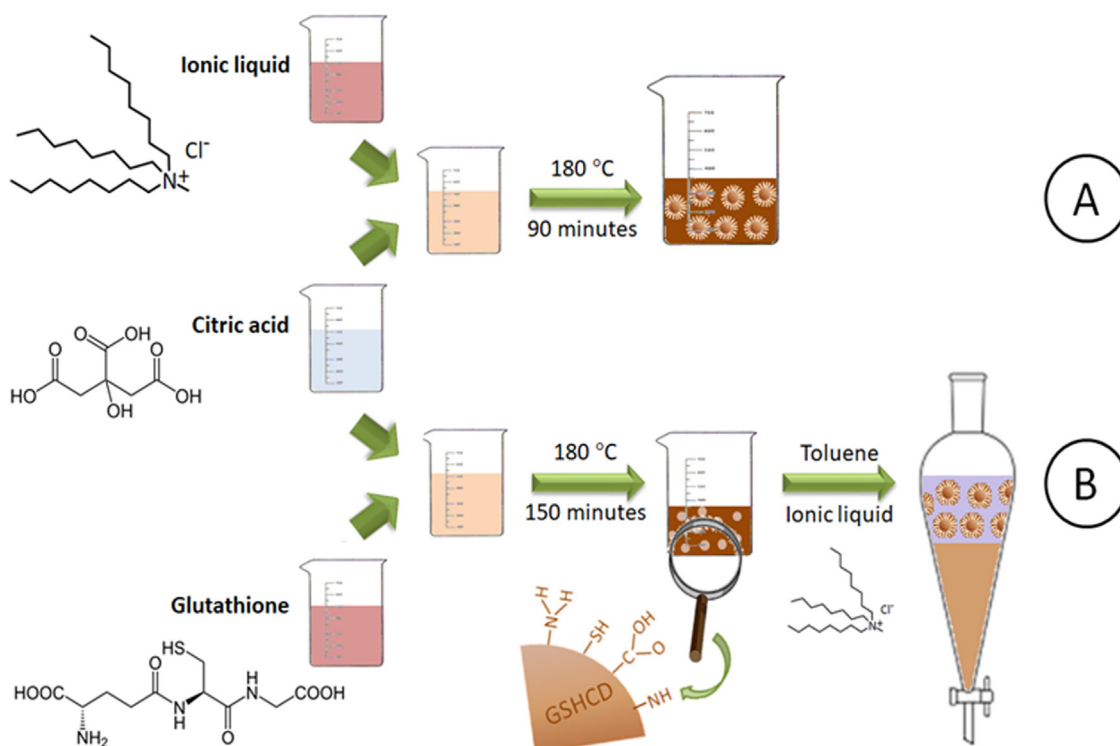
For the one-step synthesis, the remaining third of the mass was provided by the desired IL (see structures in Fig. 1S) yielding the materials MTOACDs, TBMACDs, HMICDs and MOICDs; in these materials, the ILs were not only a secondary carbon source for the synthesis of CDs but they also provided the final CDs with methyl, butyl, hexyl and octyl residues. The presence of such organic tails resulted in the formation of hydrophobic CDs that increased their distribution equilibria towards the non-aqueous media.

In the two-step approach the GSHCDs (in which the remaining third of mass was provided by glutathione) were firstly synthesized and then brought into contact with toluene solutions of the corresponding IL. Electrostatic forces between the IL and the CDs surface determine the structure of the IL-stabilized nanoparticle: each GSHCD is covered by a layer of counter-ions from IL molecules in such a way that the ionic heads form a dense surface while the hydrophobic tails remain extended into the organic media upon extraction. It was clearly observed to the naked-eye that upon extraction, the aqueous orange GSHCDs solution faded while the organic phase became brownish coloured. The final configuration of the GSHCD-IL ionic-pair can be described as an inverse micelle with the CD as the core.

The synthesis was carried out in open reactors made out of Teflon and in an oven at 180 °C, a compatible temperature with the carbonization of the citric acid whereas the thermal decomposition of the rest of reagents is negligible [27]. During the synthesis, a minimum amount of solvent was added every few minutes in order to avoid the drying of the reaction mixture.

Morphology and composition of the CDs

The obtained CDs (TBMACDs, MTOACDs, HMICDs, MOICDs, and MTOA-GSHCDs) were morphologically characterized by HRTEM and STEM. The analysis of the data provided by HRTEM images of the different CDs showed that in each case, the materials were



Scheme 1. Synthesis procedures: one-step (A) and two-steps (B) methods.

composed of monodisperse spherical particles with sizes ranging from 2.2 to 3.5 nm (Fig. 1). The presence of counter-ions on the surface of MTOA-GSHCDs did not contribute to a larger size, compared to the CDs prepared by the one-step method.

The transmittance FTIR spectra of pure imidazolium ILs (Fig. 2) revealed the presence of certain bands, which were present in the respective CDs too. Thus, bands between 3200 and 3000 cm^{-1} due to intramolecular vibrations within the imidazolium ring cation are assignable to symmetric and asymmetric stretching mode C(4/5)—H at 3153 cm^{-1} and stretching vibration C(2)—H at 3070 cm^{-1} . The intensities and frequencies are determined by the number of ion pairs and the interactions with the counter ions [28]. In the region 3000–2800 cm^{-1} appeared the common bands attributable to the ethylene groups from alkyl chains corresponding to the symmetric stretching modes (2854 cm^{-1}) and asymmetric stretching modes (2923 cm^{-1}), just like the symmetric stretching vibration of N (3)— CH_3 (2954 cm^{-1}) from the imidazole ring. The in-plane

symmetric and asymmetric stretching vibrations of C=C and N=C—N bonds of the imidazole ring were present between 1700 and 1500 and 1250–1000 cm^{-1} , respectively [29,30]. The bands between 1500 and 1200 cm^{-1} could be assigned to the C—H bonds of the alkyl chains and the imidazole ring. Bands from 800 to 600 cm^{-1} , within the ‘fingerprint region’, were assigned to C—H out-of-plane rotations and vibrations. All these bands can be observed in the spectra of HMICDs and MOICDs nanoparticles, whose surface chemistry is dominated by the ionic liquids. However, two points are worth mentioning here. First, the band at ca. 1450 cm^{-1} due C—N stretching of imidazole group present in the neat HMIC and MOIC ionic liquids practically disappeared in the corresponding CDs, which suggests strong interactions between CDs and the ILs. Second, the weak and broad band at ca. 3070 cm^{-1} observed in MOIC and HMIC spectra, due mainly to C (2)—H stretching mode [31], is absent in the spectra of MOICDs and HMICDs, suggesting that the imidazolium ion of the ILs is involved in the interaction with the CDs.

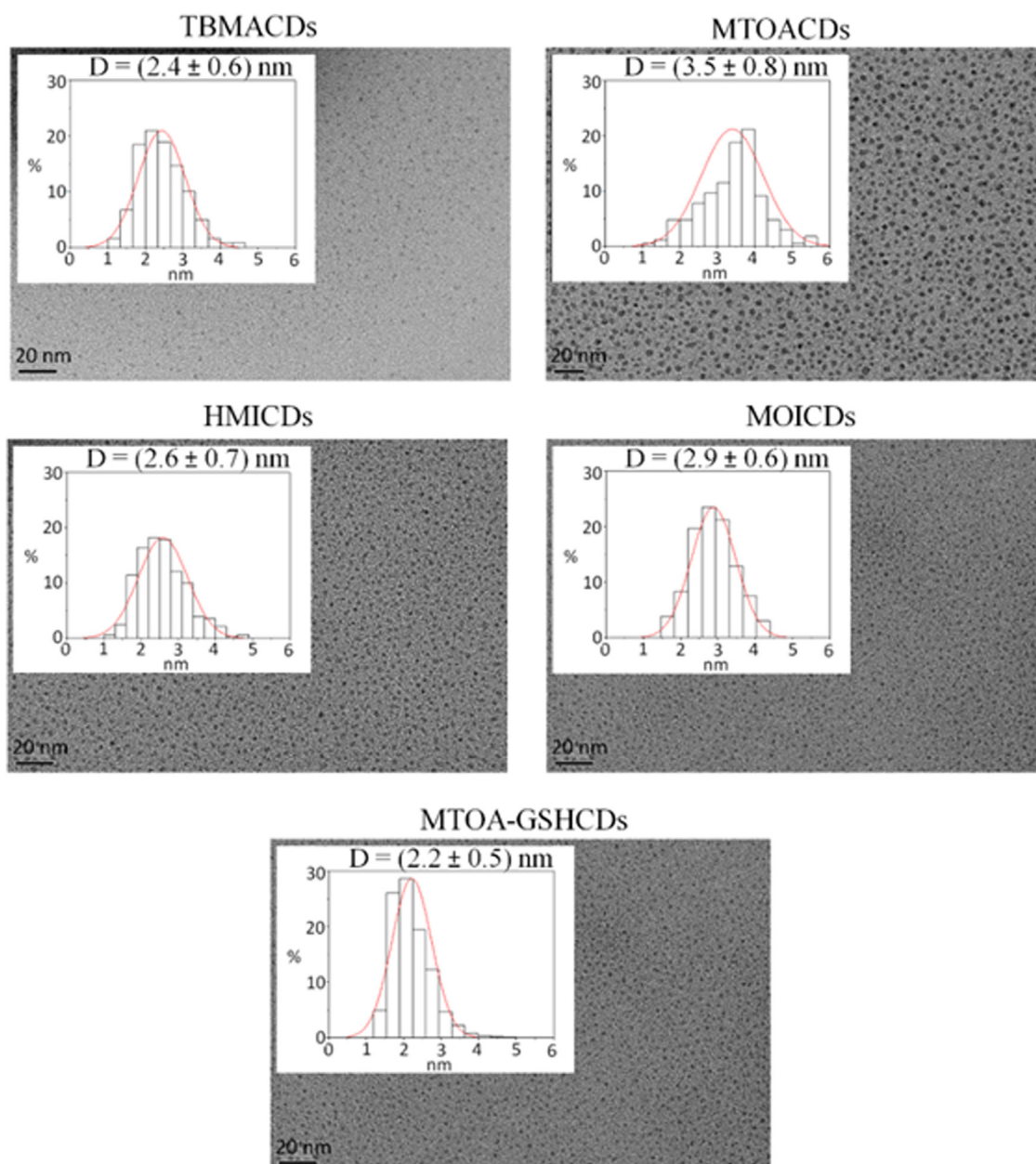


Fig. 1. HRTEM images of ethanol dispersions of nanoparticles. Inset: diameter size distribution.

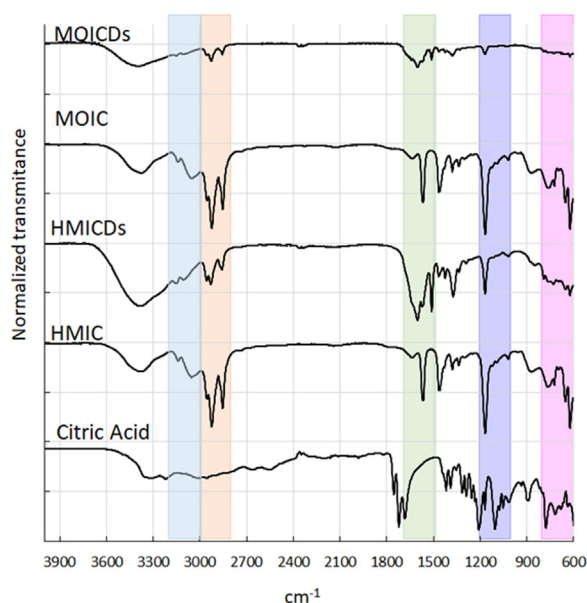


Fig. 2. ATR-FTIR spectra of the IL-based CDs synthesized and their chemical precursors.

On the other hand, the ATR-FTIR spectra of the nanomaterials obtained using alkyl-substituted ammonium ILs (Fig. 2S), either via the one-step synthesis (TBMACDs and MTOACDs) or via the two-steps synthesis (TBMA-GSHCDs and MTOA-GSHCDs), showed three bands in the region between 2990 and 2845 cm^{-1} . These positions are typical of alkyl groups (methyl, butyl and octyl). In the case of the two-step synthesis, it is interesting to note that the intense band at 1160 cm^{-1} (C—O carboxylic) of GSHCDs disappeared, most likely due to the interaction of GSHCD with ILs cations [10,29]. In summary, the ATR-FTIR spectra of the synthesized CDs revealed that the CDs surface functionalization was successfully achieved and gave good confirmation of the presence of alkyl groups able to provide CDs with a hydrophobic character.

The high resolution N1s XPS spectrum (see Table 1) for GSHCDs revealed the presence of two bands at 399.8 and 400.6 eV belonging to H—N bonds ($\sim 82\%$ total nitrogen) and C—N bonds ($\sim 18\%$ total nitrogen). This is consistent with the results for similar nanoparticles obtained by Kong et al. [32]. The N1s XPS spectra for CDs obtained from citric acid and ILs as secondary carbon source, MTOACDs and TBMACDs, were very similar showing a main peak ($\geq 94\%$ of total N) of tetra-alkyl bonded nitrogen at 402.2 and 402.1 eV for MTOACDs and TBMACDs respectively, and a small peak at 399.3 eV assigned to a minute amount of hydrogen bound to nitrogen. The high resolution N1s spectrum of MTOA-GSHCDs showed two N1s peaks at 402.1 eV (71%) and 399.5 eV (29%).

Glutathione is a linear tripeptide of L-glutamine, L-cysteine and glycine, consequently, the carbon dots obtained from it showed a higher degree of N—H (primary and secondary amine groups) rather than C—N (GSHCDs, Table 1). However, MTOACDs and TBMACDs are obtained from a carbon source with all the nitrogen present as quaternary amines and, therefore, the content of H—N

Table 1
Surface nitrogen position XPS analysis of CDs and C/N atomic relation.

	GSHCDs	MTOACDs	TBMACDs	MTOA-GSHCDs
N1s peaks	400.6 eV (18%) 399.8 eV (82%)	402.2 eV (94%) 399.4 eV (6%)	402.1 eV (97%) 399.3 eV (3%)	402.1 eV (71%) 399.5 eV (29%)
N/C ratio	7.7/100	2.4/100	3.3/100	3.3/100

was comparatively much lower while the C—N content was higher than in the case of GSHCDs (Table 1). In the case of the ionic pair MTOA-GSHCDs an intermediate position was observed, probably to a partial masking of the H—N of the GSHCDs by the quaternary amines acting as surface counter ions. The low N/C ratio in all CDs could be explained taking into account the low N/C ratio already present in the synthesis starting materials.

Visual sedimentation studies

In order to evaluate the stability of dispersions, the different CDs were dispersed in different solvents: water, ethanol and water/ethanol mixtures, as model polar media, and toluene as non-polar one and base oil (for MTOACDs and MTOA-GHSCDs). As we defined in Section “Stability of carbon dots in aqueous and hydrophobic media”, these dispersions can be considered stable whether any kind of aggregation or sedimentation was observed when left at room temperature for 15 days, provided that the CDs concentrations were $\leq 0.35\%$ (w/v). In Table 2, there is a summary of the CDs that were found to be stable in the used solvents.

The results of a visual inspection revealed that dispersions of MTOACDs, MOICDs, MTOA-GSHCDs and MOI-GSCDs, all with an octyl-modified surface, were stable in the lowest polar solvent toluene whereas suspensions of the remaining CDs bearing shorter surface alkyl chains were stable in more polar solvents or their mixtures (e.g. 20% (v/v) ethanol/water). For comparison, raw glutathione CDs were included, showing that dispersions in organic solvents were not stable.

UV-vis spectrophotometry and photoluminescence spectroscopy

The optical properties of stable dispersions of nanoparticles were investigated. The UV-vis spectra showed typical absorption bands at 240 nm attributable to $\pi\pi^*$ transitions arising from C—C bonds with sp^2 hybridization, as well as a band between 330 and 350 nm coming from $n\pi^*$ transitions of carbon – heteroatom bonds (typically O, N and S). The suspensions of GSHCDs showed photoluminescence with excitation and emission maxima at 338–347 and 419–421 nm, respectively. The estimated absolute quantum yields (Φ_{abs}) ranged from 0.47 to 0.57 in aqueous media, depending on the ionic liquid used as counter-ion (Table 3). They were obtained by detecting all sample photoluminescence through the use of an integrating hollow sphere module of 150 mm diameter. These photoluminescence characteristics are comparable to those observed by Díaz-Faes López et al. for GSHCDs ($\Phi = 0.57$, $\lambda_{\text{exc}} = 347$ nm and $\lambda_{\text{em}} = 420$ nm) [10], who measured the

Table 2
Stability of CD dispersions in solvents (0.35w/v) and based oil (0.25w/v) evaluated after 10 min sonication and a rest period of 15 days.

CDs	Solvents			Base oil
	Ethanol	Water	Toluene	BO68
<i>IL-based CDs</i>				
TBMACDs	Yes (20% (v/v) ethanol/water)			No ^a
MTOACDs	Yes	No	Yes	Yes
HMICDs	Yes	No	No	^a
MOICDs	Yes	No	Yes	^a
<i>Ion pair IL-GHSCDs</i>				
MTOA-GHSCDs	Yes	No	Yes	Yes
TBMA-GHSCDs	No	Yes	No	^a
HMI-GHSCDs	Yes	No	No	^a
MOI-GSCDs	Yes	No	Yes	^a
<i>Raw glutathione CDs</i>				
GHSCDs	No	Yes	No	No

^a The stability of nanosuspension in base oil was confirmed for the development of the measurements (about one day). However, no long-term stability experiments (15 days) were performed.

Table 3
Absolute photoluminescence quantum yield of synthesized materials.

Carbon dot	Ethanol $\Phi_{\text{abs}}, \%$	Water $\Phi_{\text{abs}}, \%$	Toluene $\Phi_{\text{abs}}, \%$
<i>IL-based CDs</i>			
TBMACD	2.36	–	–
MTOACD	3.10	–	4.11
HMICD	2.55	–	–
MOICD	3.16	–	3.28
<i>Ion pair IL-GHS based CDs</i>			
MTOA-GHSCD	6.63	–	3.95
TBMA-GHSCD	–	46.66	–
HMI-GHSCD	–	56.37	–
MOI-GSCD	–	54.05	–
GHSCD ^a	–	57.0	–

^a Data from Ref. [10].

quantum yields with a relative method, comparing the fluorescence intensity of the sample with the fluorescence of a quinine standard.

As already mentioned, the origin of the photoluminescence of CDs is not fully unveiled. Notwithstanding, according to some recent investigations on the photoluminescence origin of CDs [33–35] the chemical groups attached to the surface of CDs may induce electronic changes and modifications on the optical transition pathways through different mechanisms including surface states, quantum size effect, crosslink-enhanced emission effect and conjugated π -domains [36]. In general, upon excitation CDs photoluminescence is explained as result of electron–hole pair recombination in localized sp^2 -conjugated π -domains, considered to be the luminescent centres [37]. Several isolated π -bonds may lead to formation of such π -electron rich sp^2 -conjugated patches. CDs surface modification by passivating agents is an effective approach to enhance luminescence intensity and quantum luminescence yields through different ways: (a) preventing CDs agglomeration and, in turn, the photoluminescence quenching [38]; (b) stabilization of surface emissive π -electron rich sp^2 -conjugated systems, avoiding the migration of exciton to non-radiative energy traps at the surface/core.

Taking into account the marginal difference on the photoluminescence quantum yield (lower than 15%) observed among the ion pair IL-GSHCDs, it can be concluded that the presence of the counter IL^+ ions did not produce an effective cutting-off of non-emitting pathways into the surface of the raw GSHCDs. A plausible explanation for this observation could be related to the GSHCDs

Table 4
Properties of 'R&O' base oils used.

Property	Method	ISO 46	ISO 68
Viscosity at 100 °C	ASTM D 445	6.8 cSt	8.6 cSt
Viscosity at 40 °C	ASTM D 445	46 cSt	68 cSt
Density 15 °C	–	0.88 g cm ⁻³	0.88 g cm ⁻³
TAN	ASTM D 664	0.38 mg KOH g ⁻¹	0.38 mg KOH g ⁻¹
Flashpoint	ASTM D 92	225 °C	235 °C
Pour point	ASTM D 97	–24 °C	–24 °C
Oil chemical nature	–	PAO	PAO

TAN = total acid number.

themselves, in which passivating groups (S, N) already exist that synergistically stabilized the surface π -electron rich sp^2 -conjugated patches and, thus, additional IL^+ passivating groups did not improve the luminescence emission in aqueous media. The only role of IL^+ in ion-pair IL-GSHCDs, particularly in the case of MTOA-GSHCDs, was to improve the GSHCDs stabilization of suspensions in non-polar/organic media. On the other hand, it is worth to mention that the estimated luminescence yields fell drastically more than one order of magnitude when the MTOA-GSHCDs were in organic media (ethanol or toluene). Similar low quantum yields were also estimated for carbon nanoparticles obtained directly from the citric acid and ILs as secondary carbon source (see Table 3), indicating that these systems were equally sensitive to solvent effects.

IL-based CDs as lubricant additives

The tribological properties of those CDs suspensions considered stable in base oil as defined in Section "Stability of carbon dots in aqueous and hydrophobic media", were studied. The base oils selected for this study were Grade ISO 46 (BO46) and ISO 68 (BO68), kindly provided by REPSOL S.A. (Spain). These oils are suitable for any kind of machinery requiring 'R&O' (rust and oxidation inhibited) lubricants. Physical properties of the oils are summarized in Table 4.

The friction coefficient (CoF) and the wear (W_D) were evaluated for all the synthesized nanoparticles suspended in base oil in a 0.1% (w/v) concentration and compared to those measured for both the bare GSHCDs dispersions and the neat base oil. The assays for CoF were carried out using a ball-on-plate test in moderate conditions for a period of 20 min at room temperature with a stroke length of 4 mm at 15 Hz of reciprocating amplitude and a normal load of

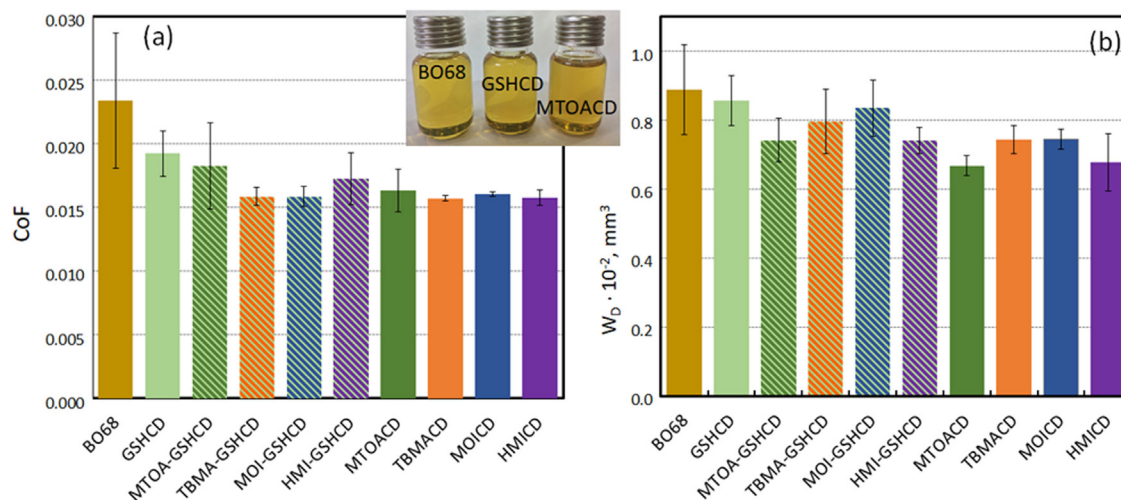


Fig. 3. Tribological properties of the different 0.1% (w/v) CDs suspensions in BO68 at 60 N: (a) friction coefficient; (b) wear.

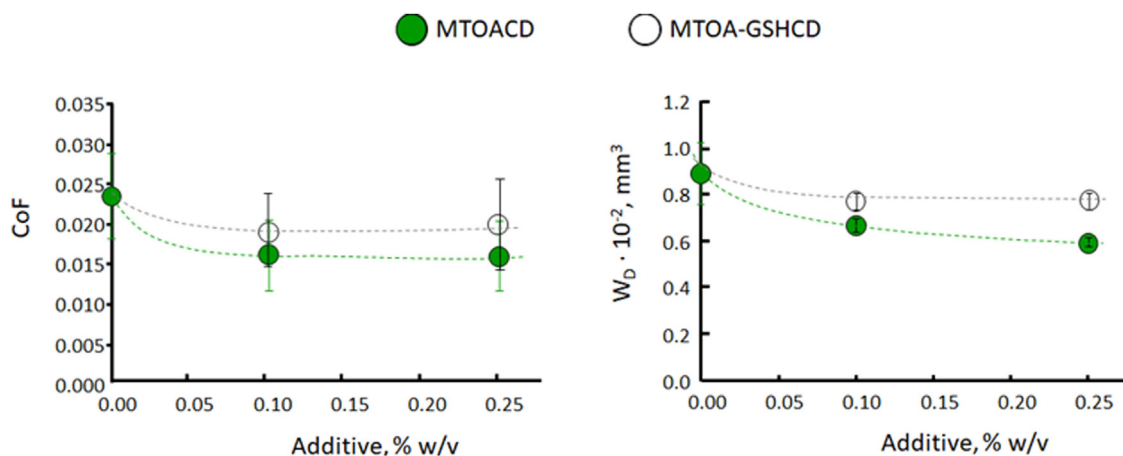


Fig. 4. Tribological properties of MTOACDs y MTOA-GSHCDs suspensions in BO68 at two different concentrations: (a) friction coefficient and (b) wear (15 Hz, 60 N, 20 min).

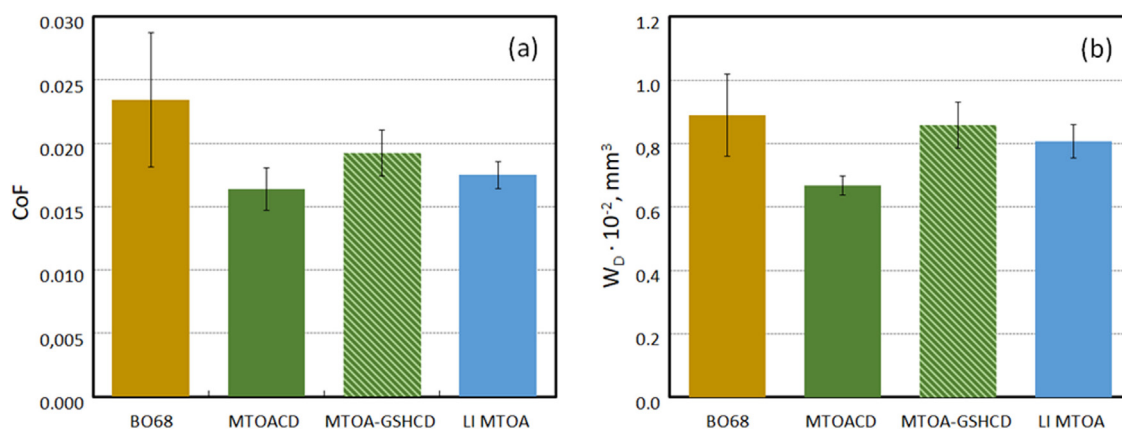


Fig. 5. Tribological properties of oil suspensions of MTOACDs (dark green) and MTOA-GSHCDs (light green) and neat MTOAC ionic liquid (blue): (a) friction coefficient and (b) wear (15 Hz, 60 N, 20 min). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

60 N. The tribological test was performed with an AISI 52,100 chrome steel ball with 9.5 mm diameter and 63 HRC (hard Rockwell scale), surface finish below 50 nm Ra (roughness average) as upper specimen and run against a softer AISI 52,100 steel disc with hardness between 190 and 210 HV₃₀ (Vickers hardness). The disc was 10 mm diameter and 3 mm thick with a surface finish below 20 nm Ra. Fig. 3a shows a clear diminution of the CoF when using

oil-CDs suspensions in comparison to the neat base oil. The oil suspensions of IL-based CDs (obtained using citric acid + IL) showed improved tribological performance characteristics than those oil suspensions of ion-pair IL-GSHCDs or suspensions of bare GSHCDs: a decrease of the CoF up to 30% was observed compared to the neat base oil. The wear was calculated considering the size of the wear scar left by the balls, while the wear volume was

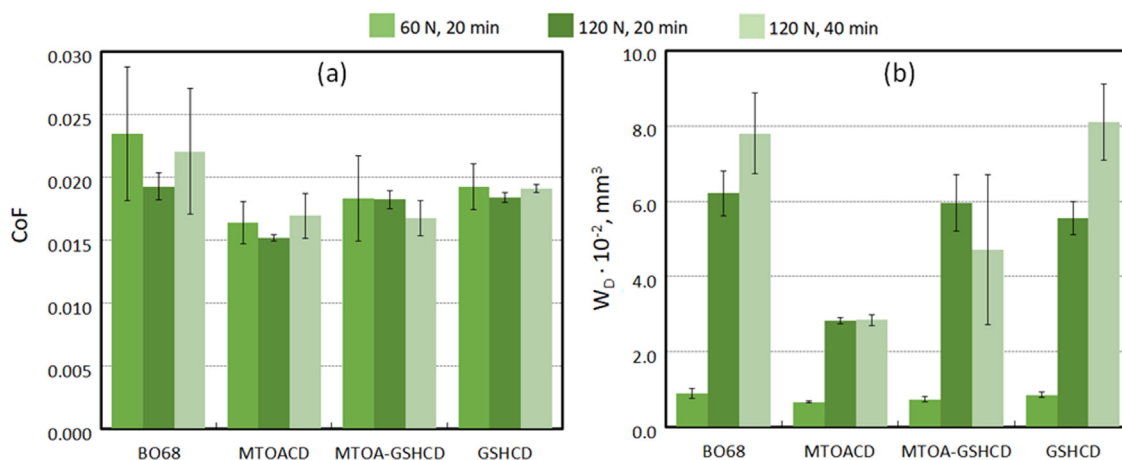


Fig. 6. Tribological properties of nanoparticles suspended in BO68 (0.10 w/v) at different load and time condition: (a) friction coefficient and (b) wear.

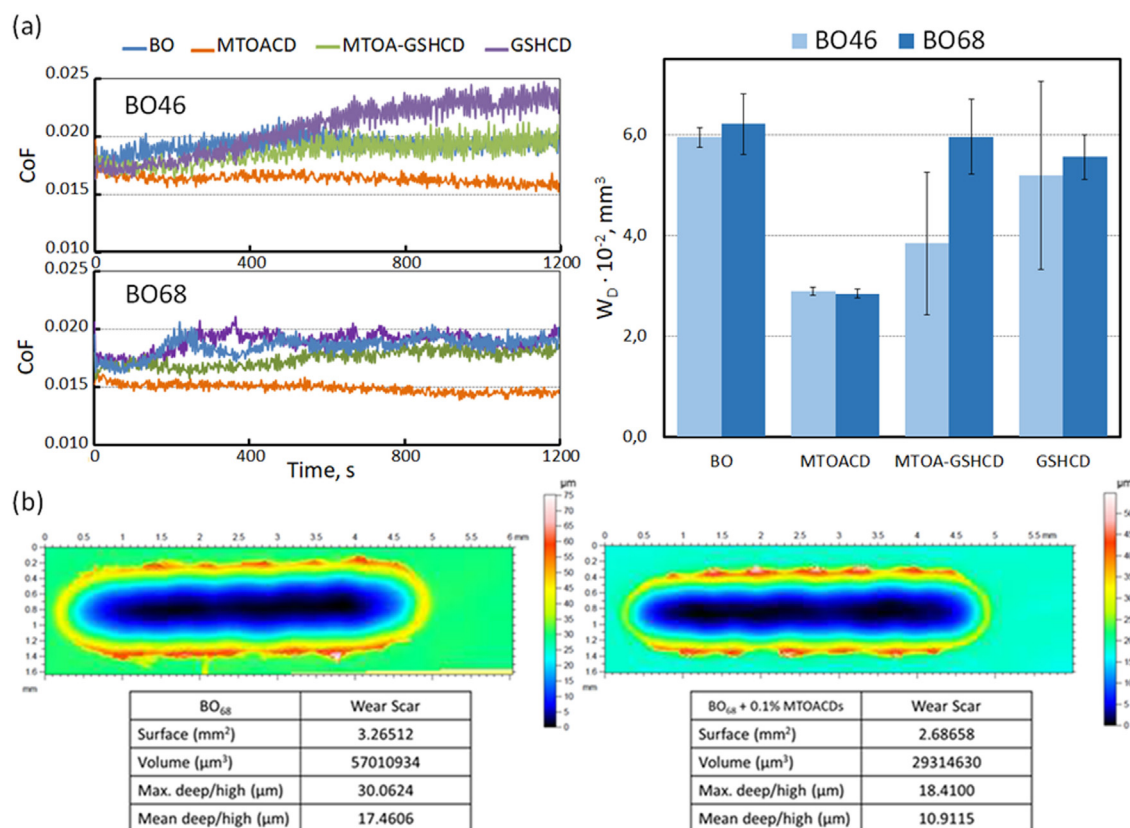


Fig. 7. (a) Tribological properties of nanoparticles suspended in BO46 and BO68 (0.10%, w/v) (left) CoF curves and (right) wear. (b) Wear surface topology comparison between BO68 and MTOACDs suspended in BO68 (0.1%, w/v) (15 Hz, 120 N, 20 min).

evaluated on the disk's surface using a confocal microscope. In this case, we found a similar behaviour among the different oily suspensions of CDs (Fig. 3b), with a reduction in the wear volume up to 14% in the best case (MTOACDs suspensions) and 3.4% in the case of the bare GSHCDs suspension.

It is worth mentioning that along with the good tribological performance of CDs as nanolubricants, their suspensions in base oils remained translucent (no precipitate formed) and without appreciable changes in the colour compared to the original base oil (see insert in Fig. 3). These characteristics contrast with other carbon-based nano-additives, whose dispersions exhibit an unwanted black colour, making the final product poorly attractive for consumers [39].

In order to compare the tribological behaviour of CDs containing similar ILs, the remaining experiments were performed using lubricant oil suspensions of MTOACDs and MTOA-GSHCDs,

that is, CDs using MTOA as secondary carbon source and ion-pair MTOA modified GSHCDs, respectively. Besides, this selection was made with the prospect of escalation to pilot plant, as the raw material is cheap (tetraalkyl ammonium ILs are cheaper than imidazolium based ILs), the obtained nanoparticles are easy to synthesize and handle, and their hydrophobicity degree provides stable oily suspensions.

As can be seen in Fig. 4, oil suspensions of MTOA-GSHCDs showed slightly poorer tribological properties compared to those of MTOACDs. An increment in the nanoparticle concentration of the suspensions from 0.10% to 0.25% (w/v) improved the wear behaviour by diminishing the wear scar in 10%, particularly for MTOACDs suspensions, as can be seen in Fig. 4.

Since the ILs have frequently been reported as additives to improve the features of lubricants [40], we also compared the tribological properties of MTOACDs with those of the neat ionic

Table 5
Comparison of performance of different CDs/ILs as additives.

CDs precursors	Surface coating precursor	Suspension concentration	Tribological test model	% COF reduced	% Wear reduced	Ref.
Citric acid MTOAC	–	0.1% (w/v) in PAO	Ball-on-plate 120 N; room temperature; 15 Hz; 20 min	21%	63% wear volumen	This work
Citric acid urea	Oleylamine	1 wt% in PAO	Four-ball 392 N; 75 °C; 1200 rpm; 60 min	47%	90% wear volumen	[41]
Citric acid	OHMimBScB	1 wt% in PEG	Four-ball 392 N; 75 °C; 1200 rpm; 60 min	73%	74% wear volumen	[42]
Glutamic acid [BHDABCO] [BScB]	–	1 wt% in PEG	Four-ball 588 N; 75 °C; 1200 rpm; 60 min	62%	89% wear volumen	[43]
Citric acid [AMIm][Br]	$\text{N}(\text{CF}_3\text{SO}_2)_2^-$	0.3 wt% in PEG	Four-ball 392 N; room temperature; 1200 rpm; 120 min	70%	33% wear scar diameter	[44]
Glucose	[Choline][Cl]	3.6% in ethylenglycol	Ball-on-disc; 20 mN; room temperature; 200 rpm	92%	86% wear rate	[24]

liquid, MTOAC. A concentration of 0.10% w/v was selected both for MTOACDs and LI MTOAC. Fig. 5 shows that both the CoF and W_D were lower with MTOACDs than with the neat MTOAC. An additional advantage of MTOACDs 0.1% (w/v) suspensions over that of 0.1% (w/v) MTOAC is its lower content of alkyl chains (lower use of IL as initial reagent), which results in lower costs and environmental impact.

The influence of the load and the time during the tribological assay was also evaluated rising the load to 120 N during 20 and 40 min. As shown in Fig. 6 the CoF was not modified significantly despite being the MTOACDs, the MTOA-GSHCDs suspensions, the neat GSHCDs and the tidy base oil under hard conditions. However, it is especially noticeable the efficiency of MTOACDs as anti-wear additive, as the wear scar was reduced ca. 63% respect to the base oil in the most severe conditions, 120 N and 40 min assay.

On the contrary, MTOA-GSHCDs and neat GSHCDs showed a negative behaviour upon the change of assay conditions, thus practically losing the anti-wear capabilities under harder experimental conditions. These results suggested that in aggressive conditions such as high load or high load/long time conditions, the degradation of both the MTOA shell and the GSHCD carbon core of the nanoparticles may take place, thus showing a similar behaviour to the neat base oil BO68.

The influence of the viscosity of the base oil in the tribological behaviour of the CDs suspensions was also evaluated. So, 0.1% (w/v) suspensions of MTOA-GSHCDs and MTOACDs in base oil BO46 were prepared. This base oil has a viscosity of 46 cSt at 40 °C (22 cSt lower than BO68). Results plotted in Fig. 7a show that MTOACDs exhibited a good anti-wear function. Fig. 7b (and Fig. 3S) show a surface topology wear comparison where it can be observed the substantial reduction in the wear when using MTOACDs suspensions, suggesting that these nanoparticles may act as a kind of 'nano-bearings' easing the sliding between the two surfaces in contact.

Table 5 summarizes these results together with other similar systems already published. It is interesting to remark that our system provides similar tribological performance as other works, despite using less than half of additive. Anyhow, it must be taken into account that the tribological conditions are different in every case and, therefore, they are comparable just to a certain extent.

The presence of octyl functional groups not only improved the dispersion ability of the nanoparticles in the base oil but also provided a way to reduce the aggregation and sedimentation phenomena. Additionally, unlike most of the nanomaterials used as additives, mainly those based in metal and/or metal oxides, the carbonaceous core of MTOA-GSHCDs and MTOACDs can act not only as an 'unctuous' or 'fluffy' protective film which minimizes the contact between the surface in a more 'friendly' way but also to trap abrasive wear particles thus protecting the surfaces from abrasive wear process. Besides, due to their size (2–3 nm) MTOA-GSHCDs and MTOACDs may have a surface positive effect by building up a physical tribo-layer to compensate for the loss of material (mending effect), thus improving the surface quality by smoothing imperfections.

Conclusions

Friction and wear studies were carried out using suspensions of different carbon dots in base oils. Carbon dots were prepared from citric acid as the main carbon source and ionic liquids as the second one. Also, carbon dots obtained from citric acid and glutathione were obtained and capped with ionic liquids through ion-pair formation. These nanomaterials showed highly interesting features, particularly as anti-wear agents. Results showed that methyltrioctylammonium chloride (MTOAC) can be used as counter ion to form ionic pairs with the glutathione based carbon

nanodots. The surrounding hydrophobic cladding proved beneficial in suspending the modified nanoparticles in base oils compared to the naked glutathione nanoparticles. Nevertheless, as the hydrophobic coating was not covalently attached, the nanomaterial lost effectivity under higher loads and longer assay times. In this case, we speculate structural changes of the dots under hard friction conditions. Further works are necessary to confirm this statement. On the other side, the carbon dots obtained directly from citric acid and ionic liquids, in particular those from MTOAC (MTOACDs) have demonstrated to be the best candidate as additive in different base oils and lubrication regimes, reducing the wear scar in more than 60% in the most extreme of the tested conditions. It is remarkable the reduction in the amount of ionic liquid necessary to obtain similar tribological features compared to the use of the pure ionic liquid itself. This not only reduces the economic costs, but also enhances the sustainability of the lubricant with a responsible use of potentially toxic compounds in the lubricants.

Conflict of interest

None declared.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jiec.2020.03.032>.

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