RSC Advances

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *RSC Adv.*, 2017, 7, 31930

Hydration or hydroxylation: direct synthesis of fullerenol from pristine fullerene [C_{60}] *via* acoustic cavitation in the presence of hydrogen peroxide

Sadia Afreen,[a] Ken Kokubo,[b] Kasturi Muthoosamy[a] and Sivakumar Manickam *[a]

Received 3rd April 2017
Accepted 4th June 2017

DOI: 10.1039/c7ra03799f

rsc.li/rsc-advances

A green and clean approach that requires low energy and avoids the use of any toxic or corrosive reagents/solvents for the synthesis of potential fullerenol moieties [$C_{60}(OH)_n \cdot mH_2O$] was proposed in this investigation, in which pristine fullerene (C_{60}) in dil. H_2O_2 (30%) aqueous media was ultrasonicated (20 kHz, 200 W) at 30% amplitude for 1 h. The attachment of hydroxyl groups (–OH) was investigated *via* FTIR and the quantification of –OH groups attached to the C_{60} cage was conducted *via* elemental analysis. The number of secondary bound water molecules (mH_2O) with each fullerenol molecule [$C_{60}(OH)_n$] was measured *via* TGA, and the estimated average structure of fullerenol was calculated to be $C_{60}(OH)_8 \cdot 2H_2O$. The synthesized fullerenol was moderately soluble in water and DMSO. Furthermore, the size of the synthesized $C_{60}(OH)_8 \cdot 2H_2O$ particles determined by both AFM and DLS analysis was found to be in the range of 135–155 nm. The proposed ultrasound-assisted acoustic cavitation technique encompasses a one-step facile reaction strategy, requires less time for the reaction, and reduces the number of solvents required for the separation and purification of $C_{60}(OH)_8 \cdot 2H_2O$, which could be scalable for the commercial synthesis of fullerenol moieties in the future.

Introduction

The discovery of fullerene (C_{60}) by Sir Harold Kroto and his group in 1985 [1,2] pioneered the new chapter of fullerene chemistry in the domain of carbon allotropes and gradually this new area of chemistry has provided versatile fullerene (C_{60}) derivatives[3] with potential features that could be exploited in numerous technological applications. Fullerene C_{60}, which is specifically known as Buckminster fullerene, is a carbon allotrope and has been incessantly reported as a useful potential carbon nanomaterial for various biological and metallurgical applications.[4–6] However, owing to its insolubility in most organic and inorganic solvents,[7,8] it is difficult to employ in many prospective studies. This tough to dissolve feature could be overcome by introducing various hydrophilic functional groups on the C_{60} cage.[9–14] Fullerenol, which is also known as fullerol, polyhydroxylated fullerene and hydroxylated fullerene, is one of the mostly pronounced and water-soluble fullerene derivatives[15] that has been derived by the hydroxylation of the C_{60} molecule in various ways (both solvent-associated and solvent-free methods) over the past few years. Ever since the first preparation of fullerenol, it has been a great challenge to increase the attachment of more hydroxyl groups (–OH) onto the C_{60} cage as well as to make the synthesis simpler and faster. The attachment of the largest number of –OH groups [$C_{60}(OH)_{44} \cdot 8H_2O$] has been reported by Kokubo *et al.*[16] Zhang *et al.*[17] reported the synthesis of $C_{60}(OH)_{27.2}$ *via* mechanochemical means where potassium hydroxide was used as the hydroxylation reagent with C_{60} and the two mixed vigorously in a ball mill. Wang *et al.*[18] reported another solvent-free reaction path to obtain $C_{60}(OH)_{16}$ using a dil. H_2O_2 (30%) and sodium hydroxide mixture. The use of alkali was very common in almost all the reported successful methods for the preparation of fullerenol together with other chemicals, *e.g.*, sulfuric acid (H_2SO_4) and nitric acid (HNO_3), various solvents *e.g.*, toluene (C_7H_8), benzene (C_6H_6) and tetrahydrofuran (THF) and phase transfer catalysts (PTC) *e.g.*, tetrabutylammonium hydroxide (TBAH).[19–21] The methods proposed by Zhang *et al.*,[22] Alves *et al.*,[23] Kokubo *et al.*,[24] Lu *et al.*,[25] Zhang *et al.*[26] and Wang *et al.*[27] to prepare fullerenols with different numbers of –OH groups are also associated with the use of H_2O_2, NaOH and in some cases PTC. However, although the previous methods were proven to be successful for the synthesis of moderate to highly soluble fullerenols, it is difficult to remove the impurities obtained from NaOH and PTC which contaminate the synthesized fullerenol.[27,28] In some cases the higher solubility of fullerenol was due to the presence of Na^+ impurity introduced during the synthesis.[23]

Also, the reaction time is much longer with these methods (from several hours to days) to generate and incorporate –OH groups onto the C_{60} cage. In this context, the development of simpler and faster approaches for the synthesis fullerenol, which

[a]*Department of Chemical & Environmental Engineering, The University of Nottingham Malaysia Campus, Jalan Broga, Semenyih, Selangor D.E., 43500, Malaysia. E-mail: Sivakumar.Manickam@nottingham.edu.my*

[b]*Division of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*

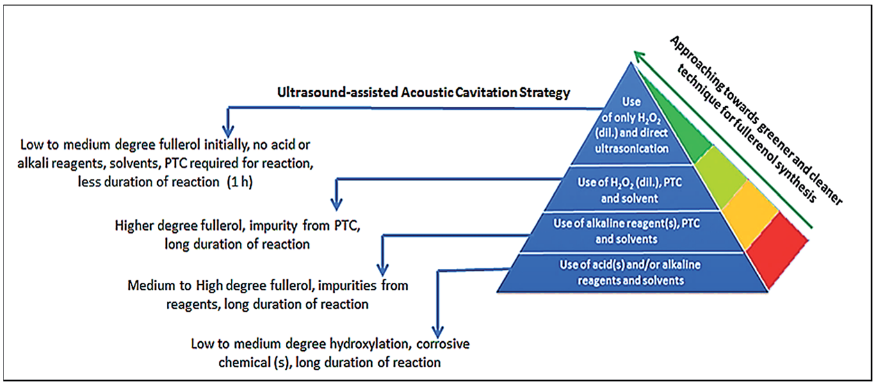

Fig. 1 Applying the greener and cleaner ultrasonic cavitation strategy to synthesize fullerenol in a facile and faster way compared to other conventional methods.

are tailored by the use of minimal reagents and customized with easy purification and separation steps, is urgently required in fullerene chemistry. In this investigation, a facile method is demonstrated to overcome the above-mentioned barriers to a great extent *via* the direct ultrasonication of C_{60} in the presence of dil. H_2O_2 (30%).

Several studies[29–31] evidence that ultrasonication in H_2O_2 associated aqueous media results in the formation of the hydroxyl radical ($^{\bullet}OH$) which generates hydrated C_{60} as $C_{60}@(H_2O)_n$.[32–34] Alternatively, it will be advantageous if the formation of $^{\bullet}OH$ radicals can be tuned to form potential fullerenol moieties as well rather than just leaving it as hydrated C_{60}. Based on this, we explore an ultrasound induced acoustic cavitation strategy whereby with optimal ultrasonic variables (30% amplitude and 1 h sonication at pulse mode), pristine C_{60} is functionalized with –OH groups in aqueous media in the presence of dil. H_2O_2 (30%). Following the synthesis, quantitative analysis is conducted with the functionalized C_{60} to determine the average structure of fullerenol that could be potentially derived by this ultrasound assisted acoustic cavitation technique.

It is worth to mentioning that the synthesis of fullerenol using H_2O_2 as a hydroxylation reagent has been practiced before, but in association with other solvents and/or reagents and PTC as well.[18,24] In this regard, herein, we propose a simpler technique which avoids the use of multiple reagents/solvents as well as PTC and thus produces fullerenol more easily and efficiently in comparison to the methods reported thus far. Fig. 1 represents the chronological development of the methods proposed for the synthesis of fullerenol over years and the salient features of the technique proposed in this study in comparison. Only dil. H_2O_2 (30%) is used as a hydroxylation reagent and no other supporting reagents and/or solvents or PTC are used for the synthesis. Besides, the reaction time is reduced to 1 h and unreacted C_{60} is only present as an impurity, the separation of which is easy after the reaction.

In the present method direct ultrasonication induces cavitation bubbles in the liquid H_2O_2 and C_{60} containing aqueous media. Continuous formation and then their collapse generate high energy transient hot spots inside the liquid media which dissociate water molecules into hydrogen and hydroxyl radicals.

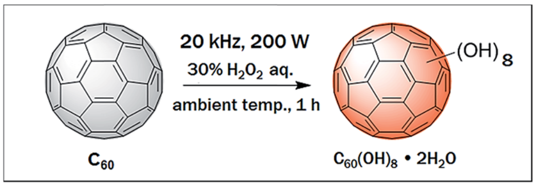

Fig. 2 Synthesis of water soluble fullerenol *via* acoustic cavitation induced by ultrasound at ambient temperature, within 1 h reaction time and in the presence of dil. H_2O_2 (30%).

These hydroxyl radicals in turn combine and form H_2O_2. Further disassociation of H_2O_2 due to the effect of acoustic cavitation generates –OOH anions and/or $^{\bullet}OH$ radicals which are exohedrally attached to the C_{60} cage by either nucleophilic attack or successive radical addition, respectively.[35–39] Fig. 2 represents the experimental conditions for the synthesis of fullerenol.

The attachment of –OH groups onto the C_{60} cage was identified by Fourier transform infrared spectroscopy (FTIR) and the number of –OH groups and bound water molecules were determined by elemental analysis and thermogravimetric analysis (TGA). The common formula of fullerenol is $C_{60}(OH)_n$, where *n* is the number of –OH groups attached to each C_{60} cage which could vary from 2 to 44.[16,24,40] However, the presence of –OH groups on the C_{60} cage also binds some water molecules, and the number of bound water molecules increases with an increase in the number of –OH groups attached to each C_{60} moiety. Therefore, the most accurate formula of the fullerenol molecule that could be obtained practically is $C_{60}(OH)_n \cdot mH_2O$,[24,39] where *m* is the number of secondary bound water molecules associated with each fullerenol moiety. Elemental analysis together with TGA clearly support that the average structure of the synthesized fullerenol obtained by the present ultrasound-assisted technique is $C_{60}(OH)_8 \cdot 2H_2O$.

Experimental

Materials & equipment

Pristine C_{60} (98%) was purchased from Sigma Aldrich (USA) and used as the starting material to synthesize fullerenol. Hydrogen peroxide (H_2O_2) aqueous solution (30% reagent grade) from

R&M chemicals (UK) was used as the hydroxylation reagent. Type II pure water (TOC < 50 ppb) was obtained from a Milli-Q system (Merck Millipore Integral 5, France). A Bandelin Sonoplus (UW 3200, 20 kHz, 200 W, Germany) with a titanium horn sonotrode (MS 73) was employed to introduce ultrasound. A graduated centrifuge tube (50 mL, angle 60° conical bottom) was used as the reactor or treatment vessel. A refrigerated circulator water bath (Julabo F34-ED, Germany) was used to maintain the reaction temperature close to ambient temperature during ultrasonication. Toluene (AR grade) was obtained from R&M Chemicals (Malaysia) for the separation and purification of unreacted C_{60} from $C_{60}(OH)_8 \cdot 2H_2O$. Dimethyl sulfoxide (DMSO) was obtained from Wako Pure Chemical Industries, Ltd (Japan) to check the solubility of synthesized fullerenol. After separation and purification, the $C_{60}(OH)_8 \cdot 2H_2O$ dispersion was dried in a freeze dryer (Christ Alpha 1-2 LDplus, Germany).

Characterization

The formation and attachment of –OH groups onto the C_{60} cage was identified by Fourier transform infrared spectroscopy (FTIR) (JASCO FT/IR-4100). Quantification of the attached –OH groups was attained by elemental analysis using a Yanaco, CHN Corder MT-6. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo instrument (TGA/DSC 1/LF/1100, Switzerland) to measure the amount of secondary bound water molecules with $C_{60}(OH)_8$. The particle size of $C_{60}(OH)_8 \cdot 2H_2O$ in solution was measured using a Photal, FPAR-1000HR. The thickness of the $C_{60}(OH)_8 \cdot 2H_2O$ particles was examined *via* a 5500 Agilent Technologies AFM (USA) using an ultra-sharp tip (non-contact high resonance frequency, nanosensor probe). The morphological study was carried out using a Quanta 400 (USA) field emission scanning electron microscope (FE-SEM).

Synthesis of $C_{60}(OH)_n \cdot mH_2O$

Pure C_{60} (200 mg) was added to 30% H_2O_2 (20 mL) and subjected to ultrasonication (30% amplitude, 200 W, pulse mode) for 1 h at ambient temperature. To avoid a rapid increase in the temperature owing to ultrasound dissipation through the liquid media, the reactor was fitted with a refrigerated circulator water bath which maintained the temperature inside the reactor close to ambient temperature. Initially, C_{60} was immiscible in aqueous H_2O_2 and was a colorless heterogeneous mixture which turned light brown after 30 min of ultrasonication. Subsequently, in the next 30 min of ultrasonication it turned into a completely dark brown dispersion (Fig. 3a).

Separation and purification of $C_{60}(OH)_n \cdot mH_2O$

Since pure C_{60} was used as the starting material to synthesize fullerenol and no other reagents were used except 30% H_2O_2 for hydroxylation, after the reaction it was easier to separate the impurity, *i.e.* unreacted C_{60}, than the reported methods. After washing the dark brown dispersion with an equal volume of toluene 10 times, unreacted C_{60} was separated from $C_{60}(OH)_n \cdot mH_2O$. After adding toluene in the dispersion, two separated layers were formed immediately; the bottom layer was dark brown and the upper layer was initially dark purple due to the dissolution of unreacted C_{60} particles into the toluene layer (pristine C_{60} is soluble in toluene and gives a purple colored solution) (Fig. 3b). Washing with toluene was repeated until the dark purple top toluene layer turned colorless, which indicated the complete removal of unreacted C_{60} from the brown layer (Fig. 3c). The dark brown dispersion containing $C_{60}(OH)_n \cdot mH_2O$ was then separated from the toluene layer and dried in a freeze dryer for 30 h (−40 °C, 0.12 mbar).

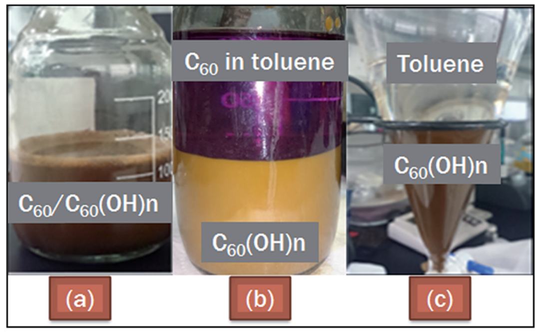

Fig. 3 (a) Dark brown dispersion immediately after ultrasonication. (b) Separation of unreacted C_{60} from $C_{60}(OH)_n \cdot mH_2O$ using toluene. (c) Clear top layer of toluene after 10 times repeated washing. Here, $n = 8$ and $m = 2$ which were finally determined by elemental analysis and TGA.

Results and discussion

Identification of –OH groups

To identify the functional group(s), the dried $C_{60}(OH)_n \cdot mH_2O$ was analyzed *via* FTIR (Fig. 4a). The clear broad peak at 3395 cm^{-1} within the range of 3600–3100 cm^{-1} indicates the characteristic O–H stretching, which does not appear in the IR spectrum of pristine C_{60} (Fig. 4b) but has been reported to be present also in the IR spectrum of pristine $C_{60}(OH)_{12}$ (Fig. 4c),[24] thus this initially confirms the attachment of –OH groups onto the C_{60} cage after functionalization.

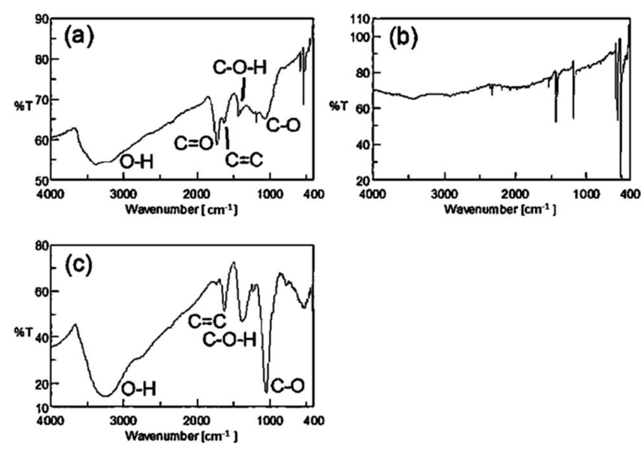

Fig. 4 FTIR spectra of (a) product $C_{60}(OH)_n \cdot mH_2O$, (b) pristine C_{60} and (c) pristine $C_{60}(OH)_{12}$.

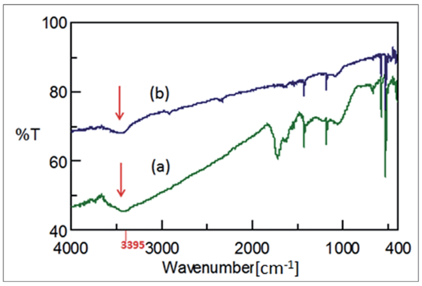

Fig. 5 IR spectra of $C_{60}(OH)_n \cdot mH_2O$ obtained *via* ultrasonication (a) in the presence of dil. H_2O_2 (30%) and (b) in type II pure H_2O without any H_2O_2.

This peak was not intense when C_{60} was ultrasonicated in type II pure water (H_2O) under the same experimental conditions but in the absence of any H_2O_2 (Fig. 5b), which indicates that the use of H_2O_2 in aqueous media is a more efficient approach to introduce –OH groups onto the C_{60} cage rather than only using H_2O for the synthesis of fullerenol in this ultrasound-assisted technique.

The peaks at 1625, 1427 and 1057 cm^{-1} (Fig. 4a and 5a) could possibly be attributed to the bond stretching of C=C, C–O–H and C–O, respectively.[41,42] Indeglia *et al.*[42] emphasized that the presence of C–O bond stretching is inevitable in all the fullerenols which perhaps indicates the formation of hemiketal groups prior to the hydroxylation of the C_{60} cage. In contrast, in the sample sonicated only with water, these significant peaks, which display the characteristic bond stretching of fullerenol, were absent in the IR spectrum (Fig. 5b), and thus also support that to synthesize fullerenol moieties *via* this ultrasound strategy the presence of H_2O_2 plays an important role in intensifying the hydroxylation. The additional peaks at 575 and 525 cm^{-1} in the finger print region (<1000 cm^{-1}) in the IR spectra of $C_{60}(OH)_n \cdot mH_2O$ (Fig. 4a and 5a) are the characteristic peaks of pure C_{60}, therefore these peaks are not attributed to any potential functional group(s). However, there could have been a trace amount of unreacted C_{60} remaining in $C_{60}(OH)_n \cdot mH_2O$ during separation and purification, which is possibly responsible for these peaks in the IR spectra of $C_{60}(OH)_n \cdot mH_2O$. We cannot rule out this possibility especially when we scale-up this method for the mass production of $C_{60}(OH)_n \cdot mH_2O$.

Estimation of the number of –OH groups and the structure of fullerenol

IR spectra alone are not enough to determine and confirm the –OH groups, their numbers and the structure of fullerenol. Therefore, elemental analysis was conducted to determine the composition and average structure of $C_{60}(OH)_n \cdot mH_2O$. The number of bound water molecules (m) within the $C_{60}(OH)_n$ structure was calculated *via* TGA. After the ultrasound-assisted functionalization of pure C_{60}, the average composition of C and O (C: 82.6 wt% and O: 17.2 wt%) in $C_{60}(OH)_n$ was first obtained from SEM-EDS analysis. In pure C_{60}, no trace of oxygen (C: 100%) was detected before the reaction which predicts the formation and presence of some oxygen containing functional group(s) in the functionalized C_{60}. However, EDS cannot analyze the presence and composition of hydrogen present in a sample. The composition and structure of $C_{60}(OH)_n$ was finally deduced from elemental analysis (Table 1).

In the elemental analysis of fullerenols if the product is a pure single isomer and can be purified totally, the difference should be within 0.4%, but generally the product fullerenol is a mixture of many isomers and it is very difficult to separate the isomers from each other. Therefore, from our many synthetic experiences, even with reaction conditions completely the same as much possible, the difference in elemental analysis is somewhat large even though the chemical and physical properties of the fullerenol are essentially the same. Due to this fact, we always judge the average molecular formula of fullerenol within 1% error of elemental analysis [Tables 1 and 2]. From elemental analysis it became evident that the number of –OH groups attached to each C_{60} cage is $n = 8$. The composition (C: 80.52%, H: 0.96%) obtained from elemental analysis is similar to that calculated theoretically for the structure of $C_{60}(OH)_8$, thus the structure of $C_{60}(OH)_n$ synthesized by the present ultrasound strategy was calculated as $C_{60}(OH)_8$ (Table 1). Similarly, elemental analysis was conducted to estimate the number of –OH groups that could possibly be attached when pristine C_{60} was sonicated in only type II pure H_2O without the addition of H_2O_2. By this method the number of –OH groups that could be attached to the C_{60} cage is only 2 ($n = 2$) (Table 2), which again supports the role of H_2O_2 in intensifying the hydroxylation.

Table 1 Empirical formula of $C_{60}(OH)_n$ synthesized in the presence of dil. H_2O_2 (30%)

	% C	% H	H_2O^a (wt%)
Experimentally obtained	80.52	0.96	5.58
Estimated average structure calculated for-			
$C_{60}(OH)_2 \cdot 8H_2O$	80.18	2.02	16.0
$C_{60}(OH)_4 \cdot 6H_2O$	80.36	1.80	12.1
$C_{60}(OH)_6 \cdot 4H_2O$	80.54	1.58	8.1
$C_{60}(OH)_8 \cdot 2H_2O$	80.72	1.35	4.0
$C_{60}(OH)_{10} \cdot 1H_2O$	79.30	1.33	2.0
$C_{60}(OH)_{10} \cdot 0H_2O$	80.91	1.13	0

[a] Measured by TGA, difference between exp. and calc. should be within ±1%.

Table 2 Empirical formula of $C_{60}(OH)_n$ synthesized only in the presence of type II pure H_2O

	% C	% H	H_2O^a (wt%)
Experimentally obtained	92.41	0.57	1.4
Estimated average structure calculated for-			
$C_{60}(OH)_2 \cdot 2H_2O$	91.14	0.76	4.6
$C_{60}(OH)_2 \cdot 1H_2O$	93.27	0.52	2.3
$C_{60}(OH)_4 \cdot 0H_2O$	91.37	0.51	0

[a] Measured by TGA, difference between exp. and calc. should be within ±1%.

The formation and attachment of –OH groups were further confirmed by TGA (Fig. 6). The weight loss (wt%) of $C_{60}(OH)_8 \cdot 2H_2O$ was observed from room temperature to 900 °C at a rate of 10 °C min^{-1} under N_2 flow at 20 mL min^{-1}.

An initial weight loss (5.58 wt%) was observed from room temperature to 100 °C which indicates the loss of bound water molecules. Since the number of –OH groups attached to the C_{60} cage is less than 10, the weight loss (5.58 wt%) for secondary bound water in $C_{60}(OH)_8$ could be observed from room temperature to 100 °C.[16] From this percentage of weight loss, the number of bound water molecules associated with each $C_{60}(OH)_8$ molecule was calculated to be 2 ($m = 2$) which is shown in Table 1 as well the estimated complete structure of the synthesized fullerenol.

After the decomposition of bound water the degradation continued to around 226 °C, which could be due to some of the intermediates such as epoxy or hemiketal oxygen and/or carbonyl oxygen generated during the ultrasound-assisted reaction.[41–43] These intermediates may be present in $C_{60}(OH)_8 \cdot 2H_2O$ in trace amounts but possibly will not hinder the characteristic physical and chemical properties of $C_{60}(OH)_8 \cdot 2H_2O$. However a detailed understanding of these intermediates present in fullerenol is not yet fully accomplished which encourages further studies. Dehydration of the –OH groups (16.85 wt%) attached to the C_{60} molecular cage mostly occurred in the second step of TGA at around 396 °C, the value of which is very close to that theoretically calculated (15.2%) for the dehydration of 8 –OH groups. The degradation observed at around 714 °C is due to the sublimation of C_{60} molecules. Together with the elemental analysis, the TGA result manifests that C_{60} could actually be successfully functionalized to fullerenol *via* ultrasound-assisted hydroxylation in the presence of aq. H_2O_2 and the average structure of the fullerenol derived from these empirical studies is $C_{60}(OH)_8 \cdot 2H_2O$.

In applying this technique for the production of fullerenol it is also necessary to explore the yield of the prepared $C_{60}(OH)_8 \cdot 2H_2O$. In this work, the yield was verified by repeating the experiment three times. The yield of $C_{60}(OH)_8 \cdot 2H_2O$ was investigated based on both the amount of $C_{60}(OH)_8 \cdot 2H_2O$ obtained after drying and the amount of unreacted C_{60} separated after reaction. The yield was found to vary between 2.18 and 4.04%. There is always a possibility of material loss during the process of drying, especially directly from the liquid state to solid state, which should be considered in any future work when reproducing the proposed method to prepare $C_{60}(OH)_8 \cdot 2H_2O$. The yield achieved is not high on the laboratory scale; however by optimizing the reaction conditions, selecting different solvents for separation and purification, improving the drying method to avoid any loss of the material, the yield of $C_{60}(OH)_8 \cdot 2H_2O$ could be increased using the proposed ultrasound method.

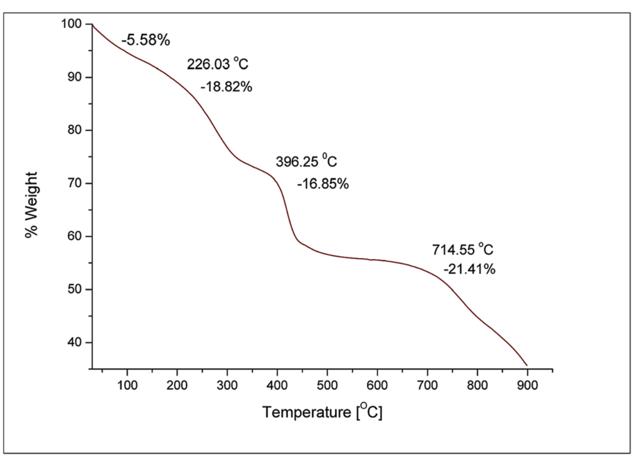

Fig. 6 TGA chart for measuring the weight loss (wt%) of $C_{60}(OH)_8 \cdot 2H_2O$.

Particle size measurements

Usually the particles of fullerenols having a fewer number of –OH groups have been reported to be aggregative and the particle size may vary in the range of 50–300 nm.[41] DLS analysis and AFM scanning were carried out to investigate the size and morphology of the $C_{60}(OH)_8 \cdot 2H_2O$ particles, respectively. For the particle size measurements, $C_{60}(OH)_8 \cdot 2H_2O$ was dissolved in DMSO (0.33 mg mL^{-1}). As a polar aprotic solvent, DMSO can dissolve both polar and nonpolar compounds. $C_{60}(OH)_8 \cdot 2H_2O$ in DMSO initially formed a suspension which was then centrifuged (TOMY, LC-200) for 5 min at 7500 rpm to obtain a clear solution of $C_{60}(OH)_8 \cdot 2H_2O$ in DMSO. Both the suspension and the solution (collected as supernatant after centrifugation) were analyzed for particle size measurements *via* the DLS method. The average particle size of $C_{60}(OH)_8 \cdot 2H_2O$ in the suspension was found to be larger (312 nm) (Fig. 7b) than that in the solution (120 nm) (Fig. 7a).

Also, larger sized particles of about 13.9 μm could be seen in the suspension (Fig. 7b) which could either be due to the highly aggregative nature of $C_{60}(OH)_8 \cdot 2H_2O$ along with some intermediates possibly present as described in the earlier section of this study or due to the presence of trace amounts of unreacted pristine C_{60} which remained in the sample after the separation process. Hence, we infer that $C_{60}(OH)_8 \cdot 2H_2O$ when dispersed in DMSO contains particles of a wider size range and thus could be considered as a polydispersed suspension, which after centrifugation provides a clear solution of uniform sized particles of $C_{60}(OH)_8 \cdot 2H_2O$ of about 120 nm. The particle size was further verified using the topography *vs.* distance chart (Fig. 8b) obtained from the AFM analysis of $C_{60}(OH)_8 \cdot 2H_2O$.

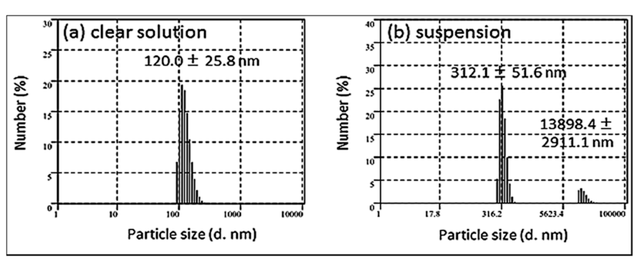

Fig. 7 Particle size measurements: (a) $C_{60}(OH)_8 \cdot 2H_2O$/DMSO solution (collected as supernatant after centrifugation) and (b) $C_{60}(OH)_8 \cdot 2H_2O$/DMSO suspension (0.33 mg mL^{-1}).

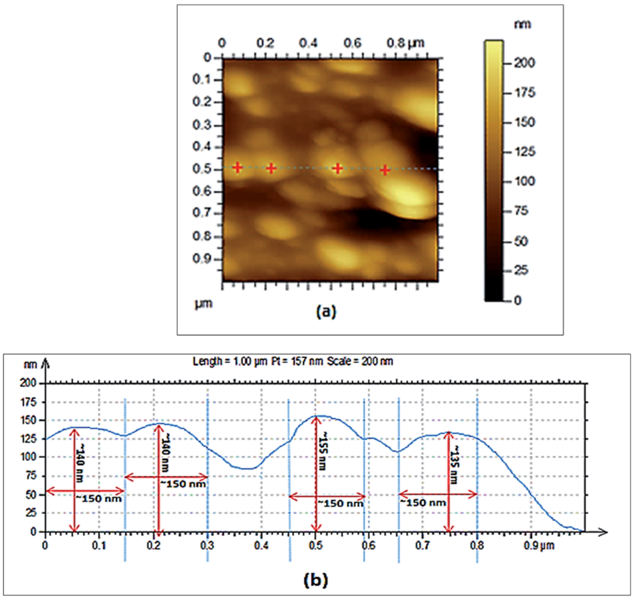

Fig. 8 (a) AFM image showing the topography of the $C_{60}(OH)_8 \cdot 2H_2O$ particles on mica substrate within a scan area of 1 µm × 1 µm; particles under the scanning line are marked with red crosses. (b) Topography *vs.* distance chart for thickness measurement, where the $C_{60}(OH)_8 \cdot 2H_2O$ particles show a consistent width of around 150 nm and the average height of the particles under scanning line is between 135 and 155 nm.

The cross section of the AFM image shows that the width of the particles is around 150 nm and their height varies from 135 to 155 nm (Fig. 8b), which indicates that the synthesized $C_{60}(OH)_8 \cdot 2H_2O$ particles could be considered spherical in shape with a diameter in the range of 135–155 nm. The average width and height of the particles obtained from the AFM analysis are congruent with the particle sizes (120 ± 25.8 nm and 312 ± 51.6 nm) obtained by DLS analysis for the saturated solution of $C_{60}(OH)_8 \cdot 2H_2O$ in DMSO (Fig. 7a) and suspension of $C_{60}(OH)_8 \cdot 2H_2O$ in DMSO (Fig. 7b), respectively. $C_{60}(OH)_8 \cdot 2H_2O$ is considered as the first member of the polyhydroxylated fullerene group to show solubility in water at a low concentration and at the same time forms aggregates when dispersed in water or DMSO. Therefore, some bigger particles are observed in the suspension of $C_{60}(OH)_8 \cdot 2H_2O$/DMSO. This aggregation is observed in both the AFM and SEM images. The image (Fig. 8a) and height profile (Fig. 8b) obtained from the AFM analysis reveal that the individual particles of $C_{60}(OH)_8 \cdot 2H_2O$ are actually not finely separated from each other, rather they are assembled in the form of nearly spherical shaped aggregates with a range of sizes.

The SEM image (Fig. 9) provides further insight into the aggregation of the synthesized $C_{60}(OH)_8 \cdot 2H_2O$ particles when they are in the powder form. In the powder form, the $C_{60}(OH)_8 \cdot 2H_2O$ particles are much more aggregative and even display sizes bigger than 300 nm, but when they are dispersed in solvent(s), aggregation is less effective. Also, this aggregation nature decreases with an increase in the number of –OH groups attached to each C_{60} molecule.[16] Even though $C_{60}(OH)_8 \cdot 2H_2O$ exhibits amphiphilic behavior, it is moderately polyhydroxylated; as a result the interaction potential between the particles becomes more effective than the intermolecular hydrogen bond potential which ultimately causes Brownian aggregation, and results in variable sizes of self-assembled $C_{60}(OH)_8 \cdot 2H_2O$ particles in the suspension.[26,44]

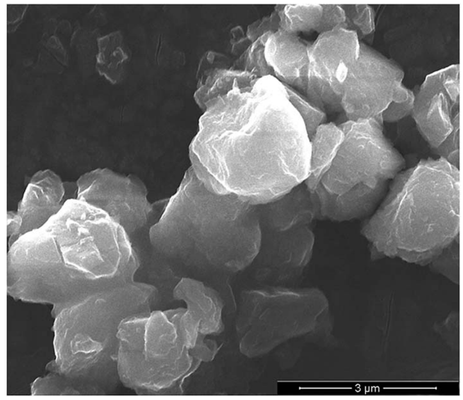

Fig. 9 SEM image of $C_{60}(OH)_8 \cdot 2H_2O$ (20 kV, magnification of 30 000×).

Color and solubility

$C_{60}(OH)_8 \cdot 2H_2O$ obtained after separation, purification and drying was not completely black, rather it was nearly brown (Fig. 10a), and when dispersed in DMSO it gave a dark brown color suspension (Fig. 10b). Fullerenol having more than 10 –OH groups is observed to be dark brown in color, which gradually shifts from dark brown to yellow with an increase in the number of –OH groups (Fig. 10c), as previously reported.[24]

The solubility of $C_{60}(OH)_8 \cdot 2H_2O$ was examined both in water and in organic solvents, *i.e.* DMSO, toluene and benzene (Table 3).

It is noteworthy to mention that $C_{60}(OH)_8 \cdot 2H_2O$ moderately dissolves in water at a lower concentration owing to its amphiphilic nature. It was found to be soluble in DMSO but did not show any solubility in toluene and benzene. On the other

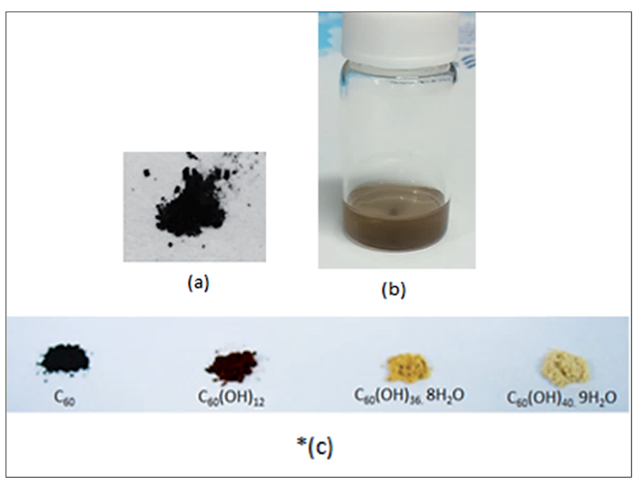

Fig. 10 (a) $C_{60}(OH)_8 \cdot 2H_2O$ after drying, (b) $C_{60}(OH)_8 \cdot 2H_2O$ in DMSO (0.33 mg mL^{-1}) and *(c) colors of different fullerenols previously reported [*reprinted from Kokubo *et al.* (ref. 24)].

Table 3 Solubility of $C_{60}(OH)_8 \cdot 2H_2O$ in comparison to C_{60} in different solvents

	Water	DMSO	Toluene	Benzene
Fullerene (C_{60})	✗	✗	O	O
Fullerenol [$C_{60}(OH)_8 \cdot 2H_2O$]	O^a	O^a	✗	✗

✗ = not soluble, O = soluble. ^{a} Soluble at lower conc.

hand, pure C_{60} dissolves both in toluene and benzene but does not show any solubility in water and DMSO.

Reaction pathways

Acoustic cavitation generated from ultrasonication results in chemical reactions inside liquid media.[45] When acoustic cavitation is induced throughout liquid media (30% H_2O_2 in this case) it produces cavitation bubbles and upon continuous ultrasonication these bubbles form and collapse randomly. The collapse of these bubbles produces transient local hot spots with intense local heat and pressure inside the liquid media which assist in high-energy chemical reactions among the molecules either trapped inside the cavitation bubbles or present in the liquid media.[46,47] In this investigation, due to ultrasound induced acoustic cavitation, radicals such as $^{\bullet}OH$, $^{\bullet}OOH$ and $^{\bullet}H$ originate from H_2O and H_2O_2 molecules.[31,48,49] Especially, the formation of $^{\bullet}OH$ radicals due to the thermal decomposition of aqueous media has been found to be evident by electron spin resonance (ESR) and spin trapping[29,30,50–52] studies. H_2O_2 is thermodynamically unstable and dissociates into H_2O and O_2 under thermal decomposition. During ultrasonic cavitation, H_2O and H_2O_2 molecules are trapped inside microbubbles, and when these bubbles collapse with the enormous amount of heat (several thousand degrees K) and pressure (hundreds of atmospheres)[53,54] the molecules decompose to $^{\bullet}OH$ and $^{\bullet}OOH$[55,56] radicals. The reaction may progress in two pathways simultaneously (Fig. 11). $^{\bullet}OH$ radicals as reactive oxygen species (ROS) attach onto the C_{60} cage to give fullerenol (Path I), and/or –OH and $^{\bullet}OOH$ radicals attack the electron deficient C_{60} double bonds in a nucleophilic reaction and this leads to the formation of fullerene epoxide [$C_{60}O_n$] as an intermediate in the first stage (Path II) which is similar to the mechanism of the Bingel reaction.[37,57] Further, the repeated attack of $^{\bullet}OH$ (or $^{\bullet}OOH$) on $C_{60}O$ *via* an S_N2 reaction results in polyhydroxylated fullerene or fullerenol.

Repeated epoxidation may take place which produces successive epoxide groups *e.g.*, $C_{60}O_2$ and $C_{60}O_3$. These epoxide groups could be possible candidates to generate other intermediates *e.g.* hydroxylated fullerene epoxide [$C_{60}(OH)_xO_y$][16,58] during sonolysis. Additionally, the subsequent ring opening of $C_{60}(OH)_xO_y$ with $^{\bullet}OH$ can result in the formation of fullerenol.[59] The formation of these intermediates during the sonolysis of H_2O_2 or H_2O in the presence of C_{60} is inevitable, and their presence in the final fullerenol (although in a trace amount) cannot go unnoted. However, because they are only present in trace amounts in the fullerenol they are not expected to cause any significant impact.

Future prospects

To explore the potential applications of fullerenols, it is indeed essential to produce high quality fullerenol which means not only higher water solubility but also free of any impurities. The presence of impurities, which generally come from the preparation process, makes fullerenol undesirable for any specific biological and metallurgical applications. More importantly, the commercial value of fullerenol depends on the presence and percentage of impurities. Moreover, a faster approach is desirable to facilitate the commercial production of fullerenol. The proposed technique for the preparation of hydroxylated C_{60} by ultrasonication in the presence of H_2O_2 is free from the use of additional hydroxylating reagents, *i.e.* NaOH, H_2SO_4, and PTC (causes impurities in fullerenol), which is a cleaner approach to produce fullerenol in an easier and a faster way. Previously, $C_{60}(OH)_{12}$ was used as a starting material to synthesize highly soluble fullerenols [$C_{60}(OH)_{36}$, $C_{60}(OH)_{40}$] by vigorously stirring

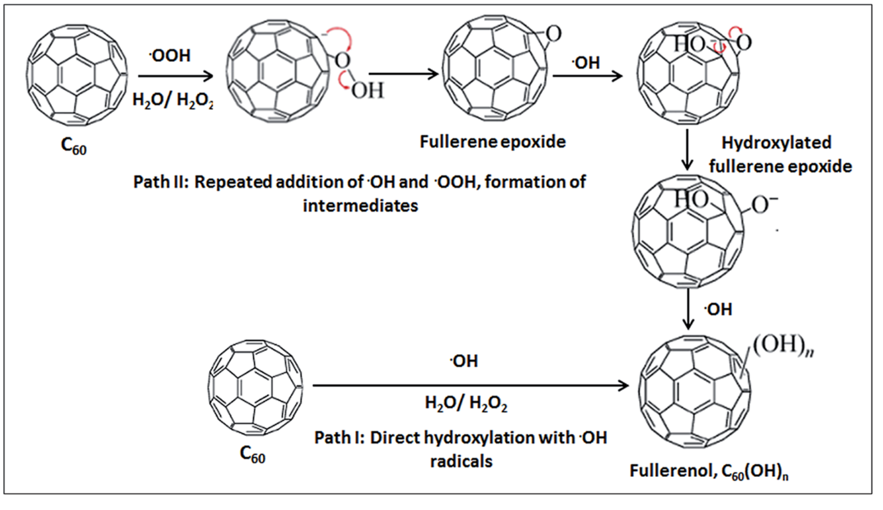

Fig. 11 Possible reaction paths in the ultrasound-assisted synthesis of fullerenol in the presence of dil. H_2O_2 (30%).

with dil. H_2O_2 for several days.[24] Similarly $C_{60}(OH)_8 \cdot 2H_2O$ synthesized by this method could be used as a starting material to further produce fullerenols containing a greater number of hydroxyl groups, *e.g.* $C_{60}(OH)_{24}$, $C_{60}(OH)_{36}$ and $C_{60}(OH)_{40}$. Moreover, compounds that express specific biochemical functions, which are required for diagnostics as well as drug therapy studies, can be derivatized from $C_{60}(OH)_8 \cdot 2H_2O$ by conjugating it with other potential functional groups or biomolecules. The conjugation of folic acid with $C_{60}(OH)_8 \cdot 2H_2O$ produced *via* this method is currently under investigation as an extended study of this work with the view to develop a highly sensitive biosensor for early stage cancer detection. Further potential applications for $C_{60}(OH)_8 \cdot 2H_2O$ synthesized by the proposed method of ultrasonication include as an antioxidant since it offers higher antioxidant activities compared to the fullerenols that have more hydroxyl groups, *i.e.*, $C_{60}(OH)_{24}$, $C_{60}(OH)_{26}$ and $C_{60}(OH)_{36}$;[39] an electrochemically active nanomediator since based on density functional theory (DFT) it has also been found that fullerenols having less hydroxyl groups are thermodynamically more stable than those containing more hydroxyl groups due to the symmetric orientation of the –OH groups around the C_{60} molecular cage;[60,61] a light harvesting material in solar cell applications[62] and the preparation of rich carbon structures of different shapes, sizes and isomeric orientations recently termed as Janus particles for various other applications.[44]

It is anticipated that there must be a substantial difference between the levels of energy generated during continuous ultrasonication and pulse mode ultrasonication which should be also addressed in future investigations. In addition, the duration of ultrasonication may cause a remarkable difference in the structure of fullerenol. Besides the variables of ultrasonication (time and power input), it is equally important to optimize the other parameters in future studies, *i.e.* temperature, size and geometry of the treatment vessel, nature and concentration of any dissolved gas, concentration of H_2O_2, solute to reagents ratio (C_{60}: 30% H_2O_2, mg mL^{-1}) and height of the mixture in the treatment vessel, where all of them alone or together can play vital roles in producing fullerenols possessing different combinations of –OH groups and bound H_2O molecules in addition to increasing the yield of $C_{60}(OH)_8 \cdot 2H_2O$ while applying the proposed ultrasound technique for the synthesis of fullerenols.

Conclusion

Herein, we have proposed a facile and fast approach to prepare fullerenol *via* the ultrasound-assisted hydroxylation of C_{60} only in dil. H_2O_2 (30%) which acts as a hydroxylating reagent and we have quantified the possible structure of fullerenol that could be derived by this technique. It appears that during the ultrasonication of pure C_{60} in aqueous media, even only in the presence of H_2O_2, not only leads to the hydration of C_{60} in the reaction media but also results in the generation of potential fullerenol candidate(s), which upon quantitative analysis has been identified as $C_{60}(OH)_8 \cdot 2H_2O$. Since no alkali, acids or PTC have been used for the synthesis, the proposed method offers a greener and cleaner approach towards the hydroxylation of the C_{60} cage compared to existing methods. Quantitative studies reveal that this hydroxylation technique assisted by ultrasonication in the presence of H_2O_2 can lead to the formation of fullerenol possessing an average structure of $C_{60}(OH)_8 \cdot 2H_2O$ and with an average yield of 2%. $C_{60}(OH)_8 \cdot 2H_2O$ was found to be amphiphilic and thus moderately soluble in water at a low concentration and it could further be exploited as a starting material to prepare highly water soluble fullerenol moieties. The presence of aq. H_2O_2 intensifies the hydroxylation and enhances the number of hydroxyl groups ($n = 8$) on the C_{60} cage in comparison to that obtained ($n = 2$) while applying the same ultrasonication but only in the presence of pure water. This indicates that H_2O_2 plays a vital role in the hydroxylation which could have potential to obtain fullerenol moieties, where the yield could be increased by varying the concentration of H_2O_2. The proposed technique encompasses a one-step reaction strategy, requires a short time for the reaction, offers a green and clean approach with a low energy requirement, avoids the use of any toxic or corrosive reagents for the synthesis, and reduces the number of solvents required for the separation and purification of $C_{60}(OH)_8 \cdot 2H_2O$. Hence, this potential approach should further be investigated to for the scale-up mass production of fullerenol moieties for a wider range of technological applications.

Author contributions

The manuscript was written through contributions of all authors.

Funding sources

Authors would like to thank Fundamental Research Grant Scheme (FRGS) for the funding support (FRGS/1/2013/SG05/UNIM/01/1).

Conflict of interest

The authors declare no competing financial interest.

Abbreviations

AFM	Atomic force microscopy
C_{60}	Fullerene
$C_{60}(OH)_n \cdot mH_2O$	Fullerenol
DMSO	Dimethyl sulfoxide
DLS	Dynamic light scattering
FE-SEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
–OH	Hydroxyl group
PTC	Phase transfer catalyst
SEM-EDS	Scanning electron microscopy with energy dispersive X-ray spectroscopy
TGA	Thermogravimetric analysis

Acknowledgements

KK thanks for the funding support by the Program for Creating Future Wisdom, Osaka University, selected in 2014. Authors would like to express their gratitude to Dr Huang Nay Ming, University of Malaya, Malaysia for carrying out AFM analysis.

References

1 H. W. Kroto, J. R. Health, S. C. O'Brien, R. F. Curl and R. E. Smalley, C_{60}: Buckminsterfullerene, *Nature*, 1985, **318**, 162–163.
2 R. E. Smalley, Discovering the Fullerenes, *Rev. Mod. Phys.*, 1997, **69**(3), 723–730.
3 S. Bosi, T. D. Ros, G. Spalluto and M. Prato, Fullerene Derivatives: an Attractive Tool for Biological Applications, *Eur. J. Med. Chem.*, 2003, **38**(11–12), 913–923.
4 M. Prato, [60]Fullerene Chemistry for Materials Science Applications, *J. Mater. Chem.*, 1997, **7**(7), 1097–1109.
5 T. D. Ros and M. Prato, Medicinal Chemistry with Fullerenes and Fullerene Derivatives, *Chem. Commun.*, 1999, 663–669.
6 N. Tagmatarchis and H. Shinohara, Fullerenes in Medicinal Chemistry and their Biological Applications, *Mini-Rev. Med. Chem.*, 2001, **1**(4), 339–348.
7 A. Hirsch, The Chemistry of the Fullerenes: An Overview, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**(8), 1138–1141.
8 N. Martın, New Challenges in Fullerene Chemistry, *Chem. Commun.*, 2006, **20**, 2093–2104.
9 I. Lamparth and A. Hirsch, Water-Soluble Malonic Acid Derivatives of C_{60} with a Defined Three-Dimensional Structure, *J. Chem. Soc., Chem. Commun.*, 1994, **14**, 1727–1728.
10 I. C. Wang, L. A. Tai, D. D. Lee, P. P. Kanakamma, C. K.-F. Shen, T.-Y. Luh, C. H. Cheng and K. C. Hwang, C_{60} and Water-Soluble Fullerene Derivatives as Antioxidants Against Radical-Initiated Lipid Peroxidation, *J. Med. Chem.*, 1999, **42**(22), 4614–4620.
11 C. F. Richardson, D. I. Schuster and S. R. Wilson, Synthesis and Characterization of Water-Soluble Amino Fullerene Derivatives, *Org. Lett.*, 2000, **2**(8), 1011–1014.
12 V. K. Periya, I. Koike, Y. Kitamura, S.-i. Iwamatsu and S. Murata, Hydrophilic [60]Fullerene Carboxylic Acid Derivatives Retaining the Original 60π Electronic System, *Tetrahedron Lett.*, 2004, **45**, 8311–8313.
13 R. Partha and J. L. Conyers, Biomedical Applications of Functionalized Fullerene-Based Nanomaterials, *Int. J. Nanomed.*, 2009, **4**, 261–275.
14 K. N. Semenov, N. A. Charykov and V. N. Keskinov, Fullerenol Synthesis and Identification. Properties of the Fullerenol Water Solutions, *J. Chem. Eng. Data*, 2011, **56**(2), 230–239.
15 A. Đorđević and G. Bogdanović, Fullerenol – a New Nanopharmaceutic?, *Arch. Oncol.*, 2008, **16**(3–4), 42–45.
16 K. Kokubo, S. Shirakawa, N. Kobayashi, H. Aoshima and T. Oshima, Facile and Scalable Synthesis of a Highly Hydroxylated Water-Soluble Fullerenol as a Single Nanoparticle, *Nano Res.*, 2011, **4**(2), 204–215.
17 P. Zhang, H. Pan, D. Liu, Z.-X. Guo, F. Zhang and D. Zhu, Effective Mechanochemical Synthesis of [60]Fullerols, *Synth. Commun.*, 2003, **33**(14), 2469–2474.
18 S. Wang, P. He, J.-M. Zhang, H. Jiang and S.-Z. Zhu, Novel and Efficient Synthesis of Water-Soluble [60]Fullerenol by Solvent-Free Reaction, *Synth. Commun.*, 2005, **35**(13), 1803–1808.
19 J. Li, A. Takeuchi, M. Ozawa, X. Li, K. Saigo and K. Kitazawa, C_{60} Fullerol Formation Catalysed by Quaternary Ammonium Hydroxides, *J. Chem. Soc., Chem. Commun.*, 1993, **23**, 1784–1785.
20 L. Y. Chiang, L.-Y. Wang, J. W. Swirczewski, S. Soled and S. Cameron, Efficient Synthesis of Polyhydroxylated Fullerene Derivatives *via* Hydrolysis of Polycyclosulfated Precursors, *J. Org. Chem.*, 1994, **59**(14), 3960–3968.
21 L. Y. Chiang, J. B. Bhonsle, L. Wang, S. F. Shu, T. M. Chang and J. R. Hwu, Efficient One-Flask Synthesis of Water-Soluble [60]Fullerenols, *Tetrahedron*, 1996, **52**(14), 4963–4972.
22 J.-M. Zhang, W. Yang, P. He and S.-Z. Zhu, Efficient and Convenient Preparation of Water-Soluble Fullerenol, *Chin. J. Chem.*, 2004, **22**(9), 1008–1011.
23 G. C. Alves, L. O. Ladeira, A. Righi, K. Krambrock, H. D. Calado, R. P. F. Gil and M. V. B. Pinheiro, Synthesis of $C_{60}(OH)_{18-20}$ in Aqueous Alkaline Solution Under O_2-Atmosphere, *J. Braz. Chem. Soc.*, 2006, **17**(6), 1186–1190.
24 K. Kokubo, K. Matsubayashi, H. Tategaki, H. Takada and T. Oshima, Facile Synthesis of Highly Water-Soluble Fullerenes More Than Half-Covered by Hydroxyl Groups, *ACS Nano*, 2008, **2**(2), 327–333.
25 Y. Lu, K. Feng, P. Qiyun and Y. Xinlin, An Improved Method for Fullerol Preparation Based on Dialysis, *Chin. J. Chem. Eng.*, 2010, **18**(5), 876–879.
26 G. Zhang, Y. Liu, D. Liang, L. Gan and Y. Li, Facile Synthesis of Isomerically Pure Fullerenols and Formation of Spherical Aggregates from $C_{60}(OH)_8$, *Angew. Chem., Int. Ed.*, 2010, **49**(31), 5293–5295.
27 F. F. Wang, N. Li, D. Tian, G. F. Xia and N. Xiao, Efficient Synthesis of Fullerenol in Anion Form for the Preparation of Electrodeposited Films, *ACS Nano*, 2010, **4**(10), 5565–5572.
28 K. Matsubayashi, K. Kokubo, H. Tategaki, S. Kawahama and T. Oshima, One-step Synthesis of Water-soluble Fullerenols Bearing Nitrogen-containing Substituents, *Fullerenes, Nanotubes, Carbon Nanostruct.*, 2009, **17**(4), 440–456.
29 K. Makino, M. M. Mossoba and P. Riesz, Chemical Effects of Ultrasound on Aqueous Solutions. Formation of Hydroxyl Radicals and Hydrogen Atoms, *J. Phys. Chem.*, 1983, **87**(8), 1369–1377.
30 X. Fang, G. Mark and C. Sonntag, OH Radical Formation by Ultrasound in Aqueous Solutions Part I: the Chemistry Underlying the Terephthalate Dosimeter, *Ultrason. Sonochem.*, 1996, **3**(1), 57–63.
31 Y. Hu, Z. Zhang and C. Yang, Measurement of Hydroxyl Radical Production in Ultrasonic Aqueous Solutions by a Novel Chemiluminescence Method, *Ultrason. Sonochem.*, 2008, **15**(5), 665–672.

32 W.-B. Ko, J.-Y. Heo, J.-H. Nam and K.-B. Lee, Synthesis of a Water-Soluble Fullerene [C60] Under Ultrasonication, *Ultrasonics*, 2004, **41**(9), 727–730.

33 R. Rivelino, A. M. Maniero, F. V. Prudente and L. S. Costa, Theoretical Calculations of the Structure and UV-Vis Absorption Spectra of Hydrated C_{60} Fullerene, *Carbon*, 2006, **44**(14), 2925–2930.

34 J. Labille, A. Masion, F. Ziarelli, J. Rose, J. Brant, F. Villiéras, M. Palletier, D. Borschneck, M. R. Wiesner and J.-Y. Bottero, Hydration and Dispersion of C60 in Aqueous Systems: The Nature of Water–Fullerene Interactions, *Langmuir*, 2009, **25**(19), 11232–11235.

35 W.-B. Ko and K.-N. Baek, The Oxidation of Fullerenes (C60, C70) with Various Oxidants under Ultrasonication, *Phys. Solid State*, 2002, **44**(3), 424–426.

36 T. H. Goswami, B. Nandan, S. Alam and G. N. Mathur, A Selective Reaction of Polyhydroxy Fullerene with Cycloaliphatic Epoxy Resin in Designing Ether Connected Epoxy Star Utilizing Fullerene as a Molecular Core, *Polymer*, 2003, **44**(11), 3209–3214.

37 W.-W. Chang, Z.-J. Li, W.-W. Yang and X. Gao, Reactions of Anionic Oxygen Nucleophiles with C_{60} Revisited, *Org. Lett.*, 2012, **14**(9), 2386–2389.

38 S.-E. Zhu, F. Li and G.-W. Wang, Mechanochemistry of Fullerenes and Related Materials, *Chem. Soc. Rev.*, 2013, **42**, 7535–7570.

39 Z. Wang, S. Wang, Z. Lu and X. Gao, Syntheses, Structures and Antioxidant Activities of Fullerenols: Knowledge Learned at the Atomistic Level, *J. Cluster Sci.*, 2015, **26**(2), 375–388.

40 M. S. Meier and J. Kiegiel, Preparation and Characterization of the Fullerene Diols 1,2-$C_{60}(OH)_2$, 1,2-$C_{70}(OH)_2$, and 5,6-$C_{70}(OH)_2$, *Org. Lett.*, 2001, **3**(11), 1717–1719.

41 L. O. Husebo, B. Sitharaman, K. Furukawa, T. Kato and L. J. Wilson, Fullerenols Revisited as Stable Radical Anions, *J. Am. Chem. Soc.*, 2004, **126**(38), 12055–12064.

42 P. A. Indeglia, A. Georgieva, V. B. Krishna and J.-C. J. Bonzongo, Physicochemical Characterization of Fullerenol and Fullerenol Synthesis By-Products Prepared in Alkaline Media, *J. Nanopart. Res.*, 2014, **16**(2599), 1–15.

43 L. Y. Chiang, R. B. Upasani, J. W. Swirczewski and S. Soled, Evidence of Hemiketals Incorporated in the Structure of Fullerols Derived from Aqueous Acid Chemistry, *J. Am. Chem. Soc.*, 1993, **115**(13), 5453–5457.

44 Y. Liu, G. Zhang, L. Niu, L. Gan and D. Liang, Assembly of Janus Fullerenol: a Novel Approach to Prepare Rich Carbon Structures, *J. Mater. Chem.*, 2011, **21**, 14864–14868.

45 J. Raso, P. Mañas, R. Pagán and F. J. Sala, Influence of Different Factors on the Output Power Transferred into Medium by Ultrasound, *Ultrason. Sonochem.*, 1999, **5**(4), 157–162.

46 K. S. Suslick and G. J. Price, Applications of Ultrasound to Materials Chemistry, *Annu. Rev. Mater. Sci.*, 1999, **29**, 295–326.

47 J. Rooze, E. V. Rebrov, J. C. Schouten and J. T. F. Keurentjes, Dissolved Gas and Ultrasonic Cavitation – a Review, *Ultrason. Sonochem.*, 2013, **20**(1), 1–11.

48 L. Villeneuve, L. Alberti, J.-P. Steghens, J.-M. Lancelin and J.-L. Mestas, Assay of Hydroxyl Radicals Generated by Focused Ultrasound, *Ultrason. Sonochem.*, 2009, **16**(3), 339–344.

49 T. J. Mason, Some Neglected or Rejected Paths in Sonochemistry – a Very Personal View, *Ultrason. Sonochem.*, 2015, **25**, 89–93.

50 G. R. Buettner, Spin Trapping: ESR Parameters of Spin Adducts 1474 1528V, *Free Radical Biol. Med.*, 1987, **3**(4), 259–303.

51 C. L. Christman, A. J. Carmichael, M. M. Mossoba and P. Riesz, Evidence for Free Radicals Produced in Aqueous Solutions by Diagnostic Ultrasound, *Ultrasonics*, 1987, **25**(1), 31–34.

52 P. Riesz and T. Kondo, Free Radical Formation Induced by Ultrasound and its Biological Implications, *Free Radical Biol. Med.*, 1992, **13**(3), 247–270.

53 C. Leonelli and T. J. Mason, Microwave and Ultrasonic Processing: Now a Realistic Option for Industry, *Chem. Eng. Process.*, 2010, **49**(9), 885–900.

54 M. Kohno, T. Mokudai, T. Ozawa and Y. Niwano, Free Radical Formation from Sonolysis of Water in the Presence of Different Gases, *J. Clin. Biochem. Nutr.*, 2011, **49**(2), 96–101.

55 C. Gong and D. P. Hart, Ultrasound Induced Cavitation and Sonochemical Yields, *J. Acoust. Soc. Am.*, 1998, **104**(5), 2675–2682.

56 G. Mark, A. Tauber, R. Laupert, H.-P. Schuchmann, D. Schulz, A. Mues and C. Sonntag, OH-Radical Formation by Ultrasound in Aqueous Solution – Part II: Terephthalate and Fricke Dosimetry and the Influence of Various Conditions on the Sonolytic Yield, *Ultrason. Sonochem.*, 1998, **5**(2), 41–52.

57 A. Hirsch, *Principles of Fullerene Reactivity. Fullerenes and Related Structures*, Springer, Berlin, Heidelberg, 1999, pp. 1–65.

58 T. H. Goswami, R. Singh, S. Alam and G. N. Mathur, Thermal analysis: a unique method to estimate the number of substituents in fullerene derivatives, *Thermochim. Acta*, 2004, **419**(1), 97–104.

59 L. Tianbao, L. Xinhai, H. Kexiong, J. Hanying and L. Jing, Synthesis and Characterization of Hydroxylated Fullerene Epoxide—an Intermediate for Forming Fullerol, *J. Cent. South Univ. Technol.*, 1999, **6**(1), 35–36.

60 X. J. Li, X. H. Yang, L. M. Song, H. J. Ren and T. Z. Tao, A DFT study on structure, stability, and optical property of fullerenols, *Struct. Chem.*, 2013, **24**(4), 1185–1192.

61 J. Zhuo, T. Wang, G. Zhang, L. Liu, L. Gan and M. Li, Salts of $C_{60}(OH)_8$ electrodeposited onto a glassy carbon electrode: surprising catalytic performance in the hydrogen evolution reaction, *Angew. Chem., Int. Ed.*, 2013, **52**(41), 10867–10870.

62 S. P. Singh, *Light Harvesting Nanomaterials*, Bentham Science Publishers, 2015.