Introduction

The discovery of fullerene (C_{60}) by Sir Harold Kroto and his group in 1985\(^1\)\(^-\)\(^4\) 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\(^5\) 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.\(^5\)\(^-\)\(^8\) However, owing to its insolubility in most organic and inorganic solvents,\(^9\)\(^-\)\(^11\) 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 fullol, polyhydroxylated fullerene and hydroxylated fullerene, is one of the mostly pronounced and water-soluble fullerene derivatives\(^15\)\(^-\)\(^18\) 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)\(_{14}\), 8H\(_2\)O] has been reported by Kokubo \textit{et al.}\(^19\)\(^-\)\(^22\) Zhang \textit{et al.}\(^23\)\(^-\)\(^26\) reported the synthesis of C_{60}(OH)\(_{16}\) via mechanoc hemical means where potassium hydroxide was used as the hydroxylation reagent with C_{60} and the two mixed vigorously in a ball mill. Wang \textit{et al.}\(^27\)\(^-\)\(^30\) reported another solvent-free reaction path to obtain C_{60}(OH)\(_{16}\) using a dil. H\(_2\)O\(_2\) (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\(_2\)SO\(_4\)) and nitric acid (HNO\(_3\)), various solvents e.g., toluene (C\(_6\)H\(_5\)), benzene (C\(_6\)H\(_6\)) and tetrahydrofuran (THF) and phase transfer catalysts (PTC) e.g., tetra-butylammonium hydroxide (TBAH).\(^31\)\(^-\)\(^34\) The methods proposed by Zhang \textit{et al.}\(^35\) Alves \textit{et al.}\(^36\) Kokubo \textit{et al.}\(^37\) Lu \textit{et al.}\(^38\) and Wang \textit{et al.}\(^39\) to prepare fullerenols with different numbers of –OH groups are also associated with the use of H\(_2\)O\(_2\), 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.\(^35\)

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
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 C₆₀ in the presence of dil. H₂O₂ (30%).

Several studies have shown evidence that ultrasonication in H₂O₂ associated aqueous media results in the formation of the hydroxyl radical (·OH) which generates hydrated C₆₀ as C₆₀(H₂O)ₙ. Alternatively, it will be advantageous if the formation of ·OH radicals can be tuned to form potential fullerol moieties as well rather than just leaving it as hydrated C₆₀. 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 C₆₀ is functionalized with –OH groups in aqueous media in the presence of dil. H₂O₂ (30%). Following the synthesis, quantitative analysis is conducted with the functionalized C₆₀ to determine the average structure of fullerol that could be potentially derived by this ultrasound assisted acoustic cavitation technique.

It is worth to mentioning that the synthesis of fullerol using H₂O₂ as a hydroxylolation reagent has been practiced before, but in association with other solvents and/or reagents and PTC as well. In this regard, herein, we propose a simpler technique which avoids the use of multiple reagents/solvents as well as PTC and thus produces fullerol 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 fullerol over years and the salient features of the technique proposed in this study in comparison. Only dil. H₂O₂ (30%) is used as a hydroxylolation 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 C₆₀ 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 H₂O₂ and C₆₀ 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.

These hydroxyl radicals in turn combine and form H₂O₂. Further disassociation of H₂O₂ due to the effect of acoustic cavitation generates ·OH anions and/or ·OH radicals which are exothermically attached to the C₆₀ cage by either nucleophile attack or successive radical addition, respectively. Fig. 2 represents the experimental conditions for the synthesis of fullerol.

The attachment of –OH groups onto the C₆₀ 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 fullerol is C₆₀(OH)ₙ where n is the number of –OH groups attached to each C₆₀ cage which could vary from 2 to 44. However, the presence of –OH groups on the C₆₀ 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 C₆₀ moiety. Therefore, the most accurate formula of the fullerol molecule that could be obtained practically is C₆₀(OH)ₙ·mH₂O·Oₘ where m is the number of secondary bound water molecules associated with each fullerol moiety. Elemental analysis together with TGA clearly support that the average structure of the synthesized fullerol obtained by the present ultrasound-assisted technique is C₆₀(OH)ₙ·2H₂O.

Experimental

Materials & equipment

Pristine C₆₀ (98%) was purchased from Sigma Aldrich (USA) and used as the starting material to synthesize fullerol. Hydrogen peroxide (H₂O₂) 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 Sonopuls (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 C60 from C60(OH)8·2H2O. Dimethyl sulfoxide (DMSO) was obtained from Wako Pure Chemical Industries, Ltd (Japan) to check the solubility of synthesized fullerene. After separation and purification, the C60(OH)8·2H2O dispersion was dried in a freeze dryer (Christ Alpha 1-2 LDplus, Germany).

Characterization

The formation and attachment of –OH groups onto the C60 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 1/1F1100, Switzerland) to measure the amount of secondary bound water molecules with C60(OH)8. The particle size of C60(OH)8·2H2O in solution was measured using a Photal, FPAR-1000HR. The thickness of the C60(OH)8·2H2O 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 C60(OH)n·mH2O

Pure C60 (200 mg) was added to 30% H2O2 (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, C60 was immiscible in aqueous H2O2 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 C60(OH)n·mH2O

Since pure C60 was used as the starting material to synthesize fullerene and no other reagents were used except 30% H2O2 for hydroxylation, after the reaction it was easier to separate the impurity, i.e. unreacted C60, than the reported methods. After washing the dark brown dispersion with an equal volume of toluene 10 times, unreacted C60 was separated from C60(OH)n·mH2O. 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 C60 particles into the toluene layer. Washing with toluene was repeated until the dark purple top toluene layer turned colorless, which indicated the complete removal of unreacted C60 from the brown layer (Fig. 3c). The dark brown dispersion containing C60(OH)n·mH2O was then separated from the toluene layer and dried in a freeze dryer for 30 h (−40 °C, 0.12 mbar).

Results and discussion

Identification of –OH groups

To identify the functional group(s), the dried C60(OH)n·mH2O 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 C60 (Fig. 4b) but has been reported to be present also in the IR spectrum of pristine C60(OH)12 (Fig. 4c), thus this initially confirms the attachment of –OH groups onto the C60 cage after functionalization.

Fig. 3 (a) Dark brown dispersion immediately after ultrasonication. (b) Separation of unreacted C60 from C60(OH)n·mH2O 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.

Fig. 4 FTIR spectra of (a) product C60(OH)n·mH2O, (b) pristine C60 and (c) pristine C60(OH)12.
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)_m•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•mH_2O during separation and purification, which is possibly responsible for these peaks in the IR spectra of C_{60}(OH)_m•mH_2O.

We cannot rule out this possibility especially when we scale-up this method for the mass production of C_{60}(OH)_n•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•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%)

<table>
<thead>
<tr>
<th>% C</th>
<th>% H</th>
<th>H_2O^a (wt%)</th>
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<tr>
<td>80.52</td>
<td>0.96</td>
<td>5.58</td>
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| Estimated obtained | 80.18 | 2.02 | 16.0 |
| Estimated structure calculated for: | 80.36 | 1.80 | 12.1 |
| C_{60}(OH)_2•8H_2O | 80.54 | 1.58 | 8.1 |
| C_{60}(OH)_4•4H_2O | 80.72 | 1.35 | 4.0 |
| C_{60}(OH)_6•2H_2O | 79.30 | 1.33 | 2.0 |
| C_{60}(OH)_{10}•1H_2O | 80.91 | 1.13 | 0 |

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

| Estimated obtained | 92.41 | 0.57 | 1.4 |
| Estimated structure calculated for: | 91.14 | 0.76 | 4.6 |
| C_{60}(OH)_2•2H_2O | 93.27 | 0.52 | 2.3 |
| C_{60}(OH)_4•1H_2O | 91.37 | 0.51 | 0 |

* 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_{2}O was observed from room temperature to 900 °C at a rate of 10 °C min⁻¹ under N₂ 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 C₆₀ 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. 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 very close to that theoretically calculated (15.2%) for C_{60}(OH)_{8}.

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.¹⁴⁻¹⁶ These intermediates may be present in C_{60}(OH)_{8} \cdot 2H_{2}O in trace amounts but possibly will not hinder the characteristic physical and chemical properties of C_{60}(OH)_{8} \cdot 2H_{2}O. However, a detailed understanding of these intermediates present in fullerenol is not yet fully accomplished which encourages further studies. Dehydration of the -OH groups (16.82 wt%) attached to the C₆₀ 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 C₆₀ molecules.

Together with the elemental analysis, the TGA result manifests that C₆₀ could actually be successfully functionalized to fullerenol via ultrasound-assisted hydroxylation in the presence of aq. H₂O₂ and the average structure of the fullerenol derived from these empirical studies is C_{60}(OH)₈ \cdot 2H₂O.

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 2H₂O. In this work, the yield was verified by repeating the experiment three times. The yield of C_{60}(OH)₈ \cdot 2H₂O was investigated based on both the amount of C_{60}(OH)₈ \cdot 2H₂O obtained after drying and the amount of unreacted C₆₀ 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 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 2H₂O. 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 2H₂O could be increased using the proposed ultrasound method.

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.¹⁴ DLS analysis and AFM scanning were carried out to investigate the size and morphology of the C_{60}(OH)₈ \cdot 2H₂O particles, respectively. For the particle size measurements, C_{60}(OH)₈ \cdot 2H₂O 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 2H₂O 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 2H₂O 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 2H₂O 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 2H₂O 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 C₆₀ which remained in the sample after the separation process. Hence, we infer that C_{60}(OH)₈ \cdot 2H₂O when dispersed in DMSO contains particles of a wider size range and thus could be considered as a polydisperse suspension, which after centrifugation provides a clear solution of uniform sized particles of C_{60}(OH)₈ \cdot 2H₂O 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 2H₂O.

Fig. 7 Particle size measurements: (a) C_{60}(OH)₈ \cdot 2H₂O/DMSO solution (collected as supernatant after centrifugation) and (b) C_{60}(OH)₈ \cdot 2H₂O/DMSO suspension (0.33 mg mL⁻¹).

Fig. 6 TGA chart for measuring the weight loss (wt%) of C_{60}(OH)₈ \cdot 2H₂O.
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}}$^2$H_{2}O 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}}$^2$H_{2}O in DMSO (Fig. 7a) and suspension of C_{60(OH)_{8}}$^2$H_{2}O in DMSO (Fig. 7b), respectively. C_{60(OH)_{8}}$^2$H_{2}O 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}}$^2$H_{2}O/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}}$^2$H_{2}O 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}}$^2$H_{2}O particles when they are in the powder form. In the powder form, the C_{60(OH)_{8}}$^2$H_{2}O 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.\textsuperscript{16} Even though C_{60(OH)_{8}}$^2$H_{2}O exhibits amphiphilic behavior, it is moderately poly-hydroxylated; 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}}$^2$H_{2}O particles in the suspension.\textsuperscript{26,44}

Color and solubility

C_{60(OH)_{8}}$^2$H_{2}O 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). Fullerol 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.\textsuperscript{24}

The solubility of C_{60(OH)_{8}}$^2$H_{2}O 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}}$^2$H_{2}O 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
Fullerenol is induced throughout liquid media (30% H2O2 in this case) ultrasound induced acoustic cavitation, radicals such as OOH and H originate from H2O and H2O2 molecules. The molecules either trapped inside the cavitation bubbles or present in the liquid media.

**Reaction pathways**

Acoustic cavitation generated from ultrasonication results in chemical reactions inside liquid media. When acoustic cavitation is induced throughout liquid media (30% H2O2 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. In this investigation, due to ultrasound induced acoustic cavitation, radicals such as 'OH, 'OOH and 'H originate from H2O and H2O2 molecules. Especially, the formation of 'OH radicals due to the thermal decomposition of aqueous media has been found to be evident by electron spin resonance (ESR) and spin trapping studies. H2O2 is thermodynamically unstable and dissociates by electron spin resonance (ESR) and spin trapping decomposition of aqueous media has been found to be evident. The molecules decompose to 'OH and 'OOH radicals. The reaction may progress in two pathways simultaneously (Fig. 11). 'OH radicals as reactive oxygen species (ROS) attack onto the C60 cage to give fullerol (Path I), and/or –OH and ‘OOH radicals attack the electron deficient C60 double bonds in a nucleophilic reaction and this leads to the formation of fullerene epoxide [C60Ox] as an intermediate in the first stage (Path II) which is similar to the mechanism of the Bingel reaction. Further, the repeated attack of ‘OH (or ‘OOH) on C60O via an S2 reaction results in polyhydroxylated fullerene or fullerol.

Repeated epoxidation may take place which produces successive epoxide groups e.g., C60O2 and C60O3. These epoxide groups could be possible candidates to generate other intermediates e.g. hydroxylated fullerene epoxide [C60(OH)xOy] during sonolysis. Additionally, the subsequent ring opening of C60(OH)2O with ‘OH can result in the formation of fullerol. The formation of these intermediates during the sonolysis of H2O2 or H2O in the presence of C60 is inevitable, and their presence in the final fullerol (although in a trace amount) cannot go unnoted. However, because they are only present in trace amounts in the fullerol 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 fullerol 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 fullerol undesirable for any specific biological and metallurgical applications. More importantly, the commercial value of fullerol depends on the presence and percentage of impurities. Moreover, a faster approach is desirable to facilitate the commercial production of fullerol. The proposed technique for the preparation of hydroxylated C60 by ultrasonication in the presence of H2O2 is free from the use of additional hydroxylating reagents, i.e. NaOH, H2SO4, and PTC (causes impurities in fullerol), which is a cleaner approach to produce fullerol in an easier and a faster way. Previously, C60(OH)12 was used as a starting material to synthesize highly soluble fullerenols [C60(OH)16, C60(OH)40] by vigorously stirring.

### Table 3  Solubility of C60(OH)x·2H2O in comparison to C60 in different solvents

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>DMSO</th>
<th>Toluene</th>
<th>Benzene</th>
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<tbody>
<tr>
<td>Fullerene (C60)</td>
<td>X</td>
<td>X</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>Fullerenol [C60(OH)3·2H2O]</td>
<td>O°a</td>
<td>O°a</td>
<td>X</td>
<td>X</td>
</tr>
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| X = not soluble, O = soluble. a Soluble at lower conc.

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Fig. 11  Possible reaction paths in the ultrasound-assisted synthesis of fullerenol in the presence of dil. H2O2 (30%).

**RSC Advances**

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with dil. H₂O₂ for several days.²⁴ Similarly C₆₀(OH)₈·2H₂O synthesized by this method could be used as a starting material to further produce fullerenols containing a greater number of hydroxyl groups, e.g. C₆₀(OH)₂₄, C₆₀(OH)₃₆ and C₆₀(OH)₄₀. Moreover, compounds that express specific biochemical functions, which are required for diagnostics as well as drug therapy studies, can be derivatized from C₆₀(OH)₈·2H₂O by conjugating it with other potential functional groups or biomolecules. The conjugation of folic acid with C₆₀(OH)₈·2H₂O 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 C₆₀(OH)₈·2H₂O 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., C₆₀(OH)₂₄, C₆₀(OH)₃₆ and C₆₀(OH)₄₀;³⁸ 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 C₆₀ molecular cage,⁶⁰,⁶¹ a light harvesting material in solar cell applications⁶² and the preparation of rich carbon structures of different shapes, sizes and isomeric orientations recently termed as Janus particles for various other applications.²⁴

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 also be addressed in future investigations. In addition, the duration of ultrasonication may cause a remarkable difference in the structure of fullerene. 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 H₂O₂, solute to reagents ratio (C₆₀: 30% H₂O₂, 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 H₂O molecules in addition to increasing the yield of C₆₀(OH)₈·2H₂O 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 C₆₀ only in dil. H₂O₂ (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 C₆₀ in aqueous media, even only in the presence of H₂O₂, not only leads to the hydration of C₆₀ in the reaction media but also results in the generation of potential fullerenol candidate(s), which upon quantitative analysis has been identified as C₆₀(OH)₈·2H₂O. 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 C₆₀ cage compared to existing methods. Quantitative studies reveal that this hydroxylation technique assisted by ultrasonication in the presence of H₂O₂ can lead to the formation of fullerene possessing an average structure of C₆₀(OH)₈·2H₂O and with an average yield of 2%. C₆₀(OH)₈·2H₂O 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 fullerene moieties. The presence of aq. H₂O₂ intensifies the hydroxylation and enhances the number of hydroxyl groups (n = 8) on the C₆₀ cage in comparison to that obtained (n = 2) while applying the same ultrasonication but only in the presence of pure water. This indicates that H₂O₂ plays a vital role in the hydroxylation which could have potential to obtain fullerene moieties, where the yield could be increased by varying the concentration of H₂O₂. 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 C₆₀(OH)₈·2H₂O. Hence, this potential approach should further be investigated to for the scale-up mass production of fullerene moieties for a wider range of technological applications.

Author contributions

The manuscript was written through contributions of all authors.

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Conflict of interest

The authors declare no competing financial interest.

Abbreviations

AFM
C₆₀
C₆₀(OH)₈·mH₂O
DMSO
DLS
FE-SEM
FTIR
–OH
PTC
SEM-EDS
TGA

Atomic force microscopy
Fullerene
Fullerenol
Dimethyl sulfoxide
Dynamic light scattering
Field emission scanning electron microscopy
Fourier transform infrared spectroscopy
Hydroxyl group
Phase transfer catalyst
Scanning electron microscopy with energy dispersive X-ray spectroscopy
Thermogravimetric analysis
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References
