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On high purity fullerenol obtained by combined dialysis and freeze-drying method with its morphostructural transition and photoluminescence

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ABSTRACT

Fullerene and its derivative fullerenol are in high demand for catalytic, electronic and biomedical applications. Here fullerenol with an estimated average structure of $C_{60}(OH)_{28}\cdot 12H_2O$ has been synthesized by a facile and scalable hydroxylation method, and distinctly, a modified purification and drying process which is hazard-free and cost-effective was employed using benzoylated dialysis tubing and lyophilizing to obtain highly pure fullerenol with high yield. More interestingly, the as-synthesized fullerenol to semi-purified fullerenol after dialysis for four days and then to fully purified fullerenol showed morphostructural transition from small and non-uniform flakes to sphere and then to perfect uniform flakes. The purified fullerenol shows tunable photoluminescence emission from violet-blue to yellowish-orange to red as we change the excitation wavelength from 240 → 285 → 350 nm. With superior optical and electronic properties, it can be made into various composites with other materials to design and develop different optoelectronic devices.

1. Introduction

Fullerene in its base form is a pure crystal form of carbon, discovered by Kroto, Curl and Smalley to whom the Nobel prize in chemistry were awarded for their seminal discovery in 1996 [1]. Its unique physical and chemical properties led researcher to explore its various technological applications such as molecular electronics [2], magnetic resonance imaging [3], photovoltaics [4], waste water treatment [5], catalysis[6], hybrid magneto-molecular optoelectronics [7], ultra-light weight multilayer armors [8], amongst many others. The main problem associated with fullerene is their extremely low solubility in water (approximately 1.3×10^{-11} mg/mL at 25 °C) which limits its applications in aqueous mediums [9]. The same poor water solubility is its main drawback for bio-medical applications. The same reason is attributed to its tendency to aggregate in water media [10]. These problems really restrict its applications for optoelectronic and medical devices. Therefore, researchers have exploited various procedures to overcome those problems, including micro-encapsulation in special carrier, co-solvent aided suspension, and chemical functionalization, etc. [11]. However, some of these methods, such as the co-solvent method, may influence the toxicity of fullerene. Chemical functionalization techniques are quite possible to covalently bind a large group of organic moieties to the fullerene cage (cage of 60 or more carbon atom) simply by (a) combining nucleophilic (Nu^-) and electrophilic (E^+) additions, (b) cyclic additions, and/or (c) radical additions. Thus, to improve the water-solubility of pristine fullerene, various fullerene derivatives have been synthesized via different chemical functionalization methods [12–15].

Among synthesized water-soluble fullerene derivatives, fullerenols (fullerols, $C_{60}(OH)_n$, $2 \le n \le 44$) have been produced by hydroxylation of fullerene molecule surface, and have attracted much attention to broad science and engineering fields because of their low toxicity, high hydrophilicity, biocompatibility, radical-scavenging ability, and antioxidant properties [16,17]. The water solubility of fullerenol depends on the amount of hydroxyl groups on the fullerene cage, exhibiting poor solubility with 12 or less hydroxyl groups and good solubility with 16 or more of them [18]. Excitingly, recent studies have shown fullerenols can be used to treat bone-loss diseases such as osteoporosis [19], as therapeutics for Alzheimer's disease [20], and anticancer agents [21]. In fact, fullerenol/alginate hydrogel was explored as injectable cell delivery vehicles for cardiac repair [22]. It has also been proposed as a potential candidate for interfacial engineering to facilitate the electron transportation in perovskite solar cells [23]. It is also reported that encapsulation of water-soluble fullerenol in supported membranes might afford “greener” membranes that could be used to design energy-efficient processes for the dehydration of acetic acid and purification of

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water [6,24].

It is well known that synthesis methods and its purification play a vital role in designing functional materials with novel properties and specific potential applications. There is no exception for fullerenol, and hence, scientists at various research groups have reported different methodologies to synthesize fullerenols and obtain high purity products. For example, Long et al. [12] have synthesized fullerenol by hydrolysis of polycyclosulfated precursors. Alves et al. have used a method wherein polyethylene glycol (PEG400) was employed as a phase-transfer catalyst between fullerene/benzene and aqueous NaOH solution [25]. Djordjevic et al. [26] have used $C_{60}Br_{24}$ as a precursor which was hydroxylated using NaOH. Most of these techniques used NaOH as the hydoxylating agent which restricts its practical application due to unwanted contamination by sodium ion [27]. There are a few other methods employing nitronium chemistry [28], hydroboration [29], solvent-free reaction of fullerene with a mixture of H_2O_2 and NaOH [30], acidic condition synthesis [31], direct reaction of fullerene with aqueous NaOH in the presence of tetrabutylammonium hydroxide (TBAH) [9], reduction of Buckminsterfullerene with Na/K alloy and successive stirring in presence of O_2 [32]. None of these methods could be able to negate the use of NaOH during the synthesis, so there is a need to design a synthesis method which can create sodium free fullerenol for its broad commercial applications.

To overcome this issue, Kokubo and co-workers used H_2O_2 as a hydroxylation reagent instead of NaOH [33]. They also explored hydroxylation of C_{60} using H_2O_2 in the presence of a phase-transfer catalyst, tetra-*n*-butylammonium hydroxide (TBAH), under organic/aqueous bilayer conditions [27]. Although Kokubo et al. have synthesized fullerenol employing sodium free hydroxylation, their method still requires the use of TBAH as a phase transfer catalyst [27]. TBAH is known to pose serious health hazard to skin and eye. To remove residual TBAH, Kokubo and coworkers used column chromatography and precipitated fullerenol thorough a mixture of 2-propanol, diethyl ether, and hexane followed by centrifugation. It is obvious that this is not a very advisable nor desirable approach as it involves the use of highly toxic chemicals as purification solvent through a time-consuming and tedious process, which also lowers the overall production yield.

To solve these problems, in this study, we investigated the possibility to develop a greener, more facile, more cost-effective and more time-efficient, but still scalable, synthesis method to obtain high purity polyhydroxylated fullerenol. Specifically, we first hydroxylated C_{60} using H_2O_2 in the presence of TBAH as the phase-transfer catalyst under organic/aqueous bilayer conditions as reported by Kokubo et al. [27], then, distinctively, modified the purification method with a combined dialysis and freeze-drying procedure as a cost-effective and hazard-free approach.

Though earlier reported processes allowed to obtain pure fullerenol, they were not friendly for human health and environment as the solvents used are often toxic. The aim of this work was to evaluate the possibility to develop a friendly method to synthesize and purify fullerenol using no solvent for extraction, green solvent and additives for purification, limiting solvent and energy consumption.

The synthesized fullerenol was then thoroughly characterized by Fourier Transform Infrared spectroscopy (FTIR), Raman spectroscopy, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), UV–Visible spectroscopy, and photoluminescence spectroscopy (PL). Our study demonstrated that this combined dialysis and freeze-drying procedure produces high purity fullerenol without the presence of used TBAH. Moreover, for the first time, we demonstrate unique morphostructural transition and photophysical properties from our synthesized fullerenol by this modified synthesis and purification technique. Related to the PL properties, the purity of a material has huge roles to play in getting good emission characteristics. Any impurity in the sample will degrade the optical emission. Such properties of our fullerenol can be further explored by making fullerenol based composite materials for optoelectronic devices and other technological applications [34–36]. Therefore, it is expected that this highly pure fullerenol with interesting properties will reinspire intense interest from the scientific and industrial communities, especially to explore their underlying properties and broad application potentials in various fields. In the present work, a novel, safer and greener approach was developed which could result in a more cost effective and scalable process. The main novel aspects that were investigated were: (i) production of highly pure fullerenol through a very simple, facile and green approach (ii) purification process based on water and (iii) interesting morphological and optical properties of synthesized Fullerenol.

2. Experimental

2.1. Chemicals and regents

All chemicals used in this study are of analytical grade reagents (AR grade) and were used without further purification. The starting materials for the synthesis of the high purity $C_{60}(OH)_n{\cdot}xH_2O$ are as follow: fullerene (C_{60}, 99.5%, Sigma-Aldrich), hydrogen peroxide (H_2O_2, 30.0%, Fisher Scientific), toluene ($C_6H_5CH_3$, 99.9%, Fisher Scientific), TBAH ($C_{16}H_{37}NO$, 40 wt% solution in water, Sigma-Aldrich), cellulose membrane dialysis tubing or benzoylated dialysis tubing (Sigma-Aldrich).

2.2. Synthesis of fullerenol

Fig. 1 shows the schematic of the synthesis procedure modified for fullerene hydroxylation and purification in our study. Specifically, our fullerenol product was first prepared with a modification to a previously reported method [27]. For example, 0.1 g fullerene was first added into 50 mL toluene and stirred in a room-temperature water bath at 700 rpms for 20 min until the mixture turned uniformly purple. And then the temperature of the water bath was set to 60 °C (Fig. 1a). Meanwhile, 10 mL of H_2O_2 and 500 μL of TBAH were added to the purple mixture. Once the temperature reached 60 °C, the mixture was kept under stirring overnight (~16 h). After stopping the stirring, the mixture was cooled down to room temperature, and a phase separation occurred. More specifically, a bilayer mixture was obtained with a colorless transparent toluene layer on the top and a dark yellow fullerenol layer on the bottom (Fig. 1b). Then the fullerenol layer was separated out by a separation funnel from the bilayer mixture, and then transferred in a cellulose membrane dialysis tubing or benzoylated dialysis tubing. The dialysis of TBAH out of the tubing from the fullerenol lasted for six days in DI water while water was replaced daily. For the purification of the fullerenol product from TBAH, which was used as the phase transfer catalyst during the conversion of fullerene into fullerenol, for our study here, the work zone of the aqueous fullerenol ($C_{60}OH_{24\text{-}28}$) solution was within ~150 h before major agglomeration occurs. The length of the work zone is dependent on the hydroxylation degree of the fullerene for which a higher degree provides a longer work zone [37]. Thereafter, the dialyzed fullerenol sample was placed in a centrifuge tube and stored at −83 °C for 24 h, then the frozen sample was placed in a Labconco Freeze Dry System until it was fully dried. This newly developed purification and drying method, i.e. our combined dialysis and freeze-drying procedure, gave a yellow high-purity fullerenol powder (Fig. 1c). In terms of purity, non-purified fullerenol is not free flowing and they tends to agglomerize, which can also be seen from the schematic shown in Fig. 1. To confirm that TBAH is purified from the initial fullerenol layer and demonstrate that further dialysis is not necessary after 6 days, re-dialysis of the frozen dried samples was undertaken. Similar Fourier transform infrared (FTIR) characteristics of the samples (Fig. S1, ESI#) confirm that the obtained fullerenol was fully purified through the first 6-day dialysis and a second time dialysis is not needed to further purify the fullerenol sample.