Review on Silica-Fullerene Hybrid Materials: Synthesis, Properties and Applications*

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Abstract:

Fullerenes have demonstrated applications in various fields. Use of fullerenes in optical devices has been studied. Due to thermal instability, ability to form clusters and sparing solubility of fullerenes had imposed the direct use of these materials. In contrast, when doped with another host materials, such as silica, polymers, metal clusters, they gain practical value. In this paper, the synthesis, optical properties and applications of fullerene-silica hybrid materials are discussed. The synthesis was carried out by sol-gel processing. The optical limiting behavior of these materials was observed. Optical properties were typically measured using UV/Vis and photoluminescence. The high damage threshold makes it possible to use such hybrids in laser applications.

Key Words: Silica, fullerene, sol-gel, optical materials, optical limiting.

Introduction:

Buckminster fullerene also called bucky ball is a distinct state of carbon. They were reported by Kroto *et al.* in the form of C_{60} molecules [1]. Since then there have been various studies for the utilization of this physically stable but chemically reactive molecule. Applications of C_{60} in areas such as optical devices, semiconductors, chemical sensors, catalysis and in the medical field have been predicted [2].

Fullerenes possess optical limiting properties due to reverse saturable absorption (RSA). Such properties are also seen in metallo-phthalocyanines and metal clusters but fullerenes are preferred due to their broader ground and excited state spectra [3]. In spite of these properties, low solubility, thermal instability and tendency to form clusters have restricted the applications of fullerenes up to a greater extent.

In contrast, when they are mixed with a host material, such as polymers, metals, they can be of practical use. Organic polymers are thermally instable than inorganic polymers that are not only stable but also durable [4]. Silica gel, an inorganic polymer, has a three-dimensional network and can be easily synthesized via sol-gel route [5]. Another reason for the use of silica glasses is their high transmittance (~100%) [3]. Thus silica-C_{60}

* Submitted as a Review of One Application of Nano-structured Powders for the Nano-Structured Powders: Synthesis, Structure and Applications course

Some of the information belongs to SJC research group, MSE, UC.

hybrid materials can be synthesized by sol-gel processing and may lead to the development of stable and durable glasses [4]. As mentioned above, due to the low solubility, fullerenes cannot be incorporated into sol-gel glasses homogeneously. In addition, they form clusters, which further reduces the quality of the product.

These problems can be overcome by functionalization of the fullerenes with such groups that will form some kind of bond (hydrogen bonds, van der Waals attractions or chemical bonds) with the growing silica network. Hence a reasonable homogeneous material can be obtained.

The synthesis of silica-fullerene hybrid materials is achieved by sol-gel processing, as mentioned above. Silica precursor is typically mixed with an alcohol and water. Acid is added as a catalyst. Fullerene are then added to this mixture directly or by dissolving in toluene. The mixture is allowed to gel over a period of time at elevated temperature. Glass monoliths are thus obtained and characterized [3, 4, 6-9]. Another scheme for synthesis of such hybrids have been demonstrated recently [10]. This process also adopts sol-gel processing, but the process conditions are very mild (20^0C, ambient pressure and in aqueous medium) such that they have economical advantage over aforesaid processes.

Applications of these materials are in the field of optical limiting devices and will be discussed below.

Synthesis:

C_{60} was incorporated in poly(methyl methacrylate) (PMMA) and the properties of this hybrid material were studied. The optical-limiting performance of the C_{60} hybrids was reasonable but they had a low damage threshold (2 J/cm^2) [8]. Thus silica was a potential material and was then studied.

Initially, attempts were made to incorporate non-functionalized fullerene into silica matrix by mere physical mixing. The poor solubility caused phase separation problems resulting in the heterogeneous product. The formation of considerable clusters was observed in such products [6, 7, 9].

Further, fullerenes were functionalized as shown in Figure 1. The side groups mainly consisted of nitrogen or Si-O-R groups (R = Me, Et) or even hydroxyl groups [3, 4]. The purpose of the presence of the silicon-alkoxide group was justified as the formation chemical linking of the dopant (fullerene) with the silica matrix, but no such evidence was provided [3, 8].

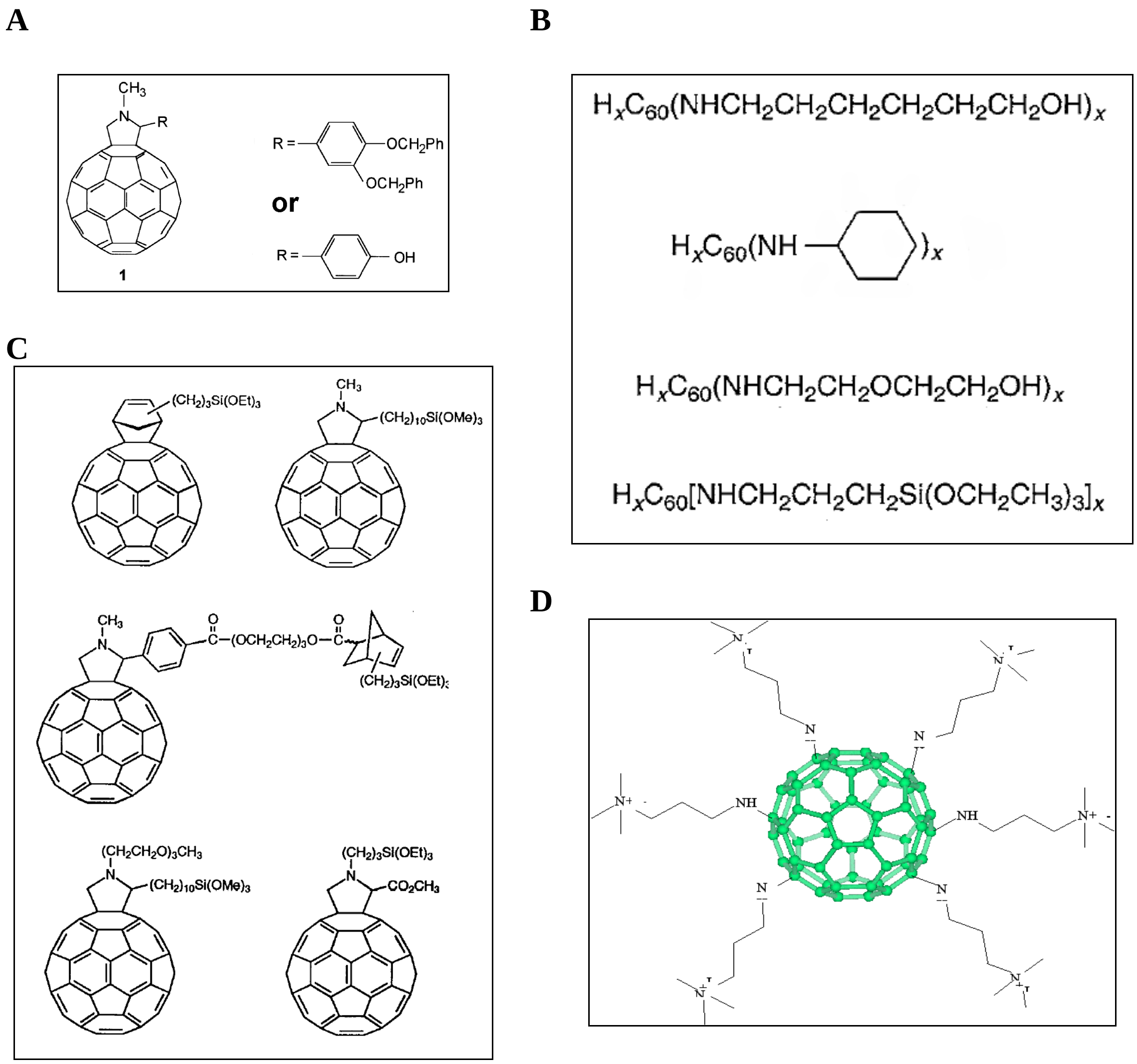

Figure 1. *Various schemes of functionalized C_{60} (reproduced from A ref. 3, B ref. 4, C ref. 8 and D ref. 10).*

The synthesis is divided into to schemes:

(*1*) Typical synthesis scheme [4] followed more or less by others [3, 6-9] is as follows. A reaction mixture was prepared by adding TEOS, ethanol, water, HCl, C_{60} solution of desired strength, in toluene and additives, if any (that include drying control agents [4]). The reaction mixture, which was at acidic medium, was stirred, heated to ~ 60^{0}C and was left for several hours, even months in some cases, for gelation. Upon formation of a monolith gel, drying was undertaken and the product was characterized.

(*2*) Another method under ambient conditions, as mentioned above, was carried out as follows. To a pre-hydrolyzed tetramethoxysilane (TMOS) solution, an aqueous solution of functionalized fullerene, as shown in the Figure 1D, of desired concentration, was added. The mixture was then buffered to pH 7.0. After 5 minutes, the reaction solution was centrifuged, washed with deionized ultrafiltered water and diluted to avoid further reaction. The sample was then dried under ambient conditioned and was then characterized. Typical sample seen under SEM is shown in Figure 2 [10]. The functionalized fullerene had a nitrogen end group that was quadra-substituted. When mixed with water, it protonates and thus dissolves forming a homogeneous solution. This allows the sol-gel processing and the synthesis of homogeneous material.

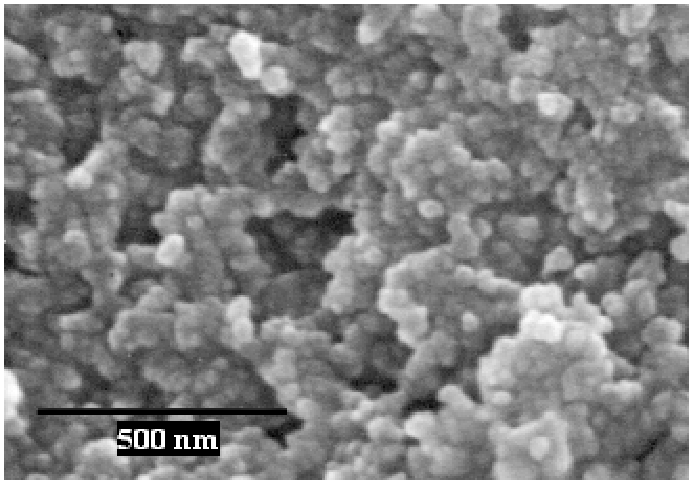

Figure 2. *Representative SEM of silica-C_{60} hybrid synthesized by scheme* ***2*** *(reproduced from ref. 10).*

As seen above, the synthesis scheme ***1*** requires rather harsh process conditions, unlike the ambient conditions of the process ***2***. In additions, none of the products obtained from procedure ***1*** were studied for morphological details.

Properties:

Optical limiters are explained as:

> "*Passive devices based on some kind of smart material that exhibits a high linear transmission at low energy inputs, but strongly and quickly reduces its transmittance when the intensity of the laser pulse approaches dangerous levels*" [8].

Whether or not these properties were achieved in the products obtained by aforesaid synthesis, was then investigated and is described below.

The products were characterized using FTIR [7] and UV/ Vis [3, 6]. Typical results are shown in Figure 3 and 4 respectively. Characteristic peaks of C_{60} around 530, 575, 1180, 1430 cm^{-1} are seen in FTIR (Figure 3) [7]. In addition, the absorption around 260 and 330 nm was observed in UV/Vis spectra [3]. These results indicate that the C_{60} fullerenes were incorporated in the silica matrix and their structure and hence the functionality was retained even after sol-gel processing. The UV/ Vis spectra continuously red shifted [4]. Also, as the fullerene concentration increased, the luminescent intensity decreased and the peaks became broader and red-shifted [7]. These facts indicate that even though functionalized, fullerenes show a tendency of cluster formation, thus creating inhomogeneity in the product.

The silica-C_{60} hybrids were stable under continuous attack of strong laser pulses and it was observed that even then optical limiting power of these hybrids was retained [4]. The hybrid sol-gel glasses were also found to be thermally stabile, which was thought to be the property of the silica retained in the final product [4].

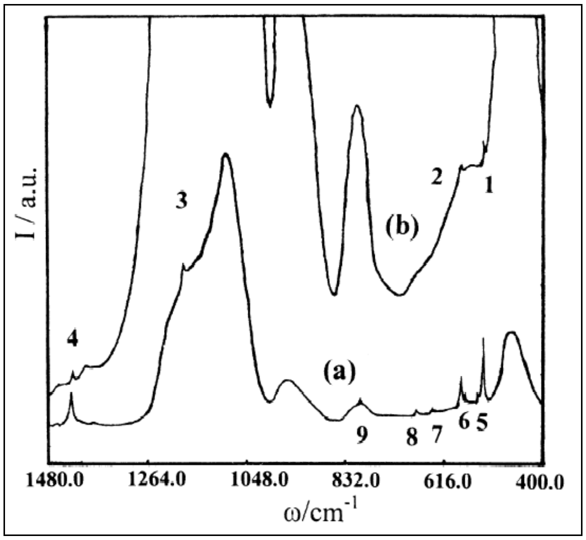

Figure 3. *FTIR of Silica-C_{60} (reproduced from ref. 7). (a) C_{60} added to sol-gel mixture and (b) C_{60} added to sol-gel mixture by dissolving in toluene.*

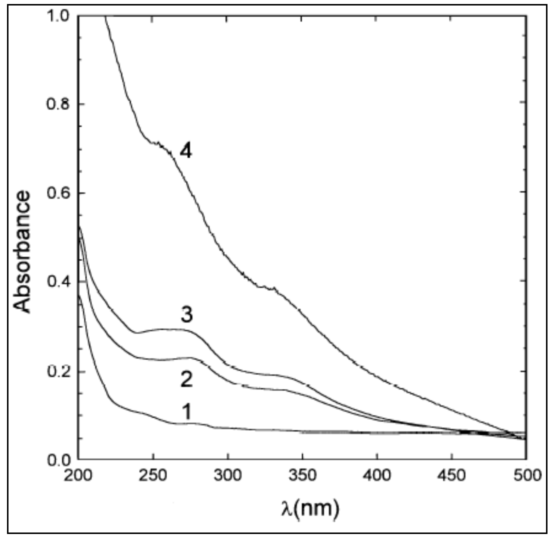

Figure 4. *UV/Vis of Silica-C_{60} (reproduced from ref. 3). 1. Silica films, 2and 3. Silica doped with compounds of Figure 1A and 4. Powdered film containing C_{60} and KBr.*

The optical limiting characteristics of the products were studied and are shown in Figure 5 [3]. The absorbance of the product was similar to that obtained for fullerene solutions [8]. Non-linear absorption of the product shows the OL effect due to C_{60}, and is related to the concentration of C_{60} in the matrix [3]. The damage threshold was seen to be ~ 30 J/cm^2 (compare with that of PMMA matrix: 2 J/cm^2) [8].

The concentration of the fullerene also affected the color of the product and was reported as follows [4]:

> *$H_xC_{60}[NH(CH_2)_6OH]_x$/SiO2 glasses (see Figure 1B) were homogeneous and transparent, although their C_{60} contents were much higher as compared to ~0.01% C_{60} when non-functionalized fullerene was used. When the C_{60} content was 0.11%, the glass was light yellow in color; when the C_{60} content was increased to 0.55%, the color changed to deep red.*

We can make use of this result for designing color of a material by just using an appropriate amount of C_{60} [4].

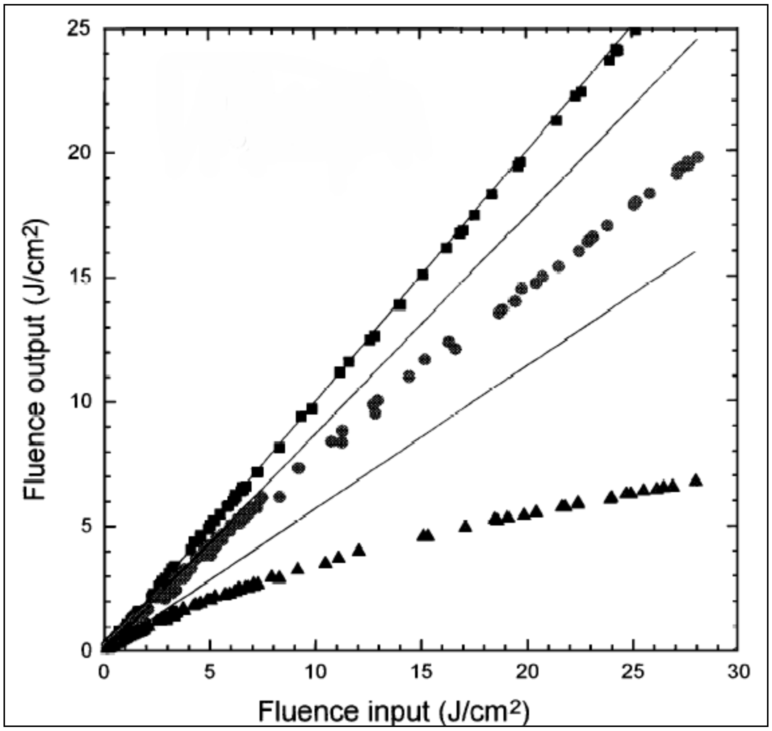

Figure 5. *Optical Limiting data of (■) pure silica, (●) silica + C_{60} and (▲) silica+ compound 1A from Figure 1.*

Applications:

These hybrid materials may have applications in areas such as optical devices, semiconductors, chemical sensors, catalysis and in the medical field [2].

Strong absorption in the UV region, by the C_{60}, and weak absorption over visible region makes them useful in optical limiting materials. As discussed above, when doped in silica matrix, they retain these properties. In addition, they gain from the matrix, the thermal stability and stability against laser attack. Thus, they can be used in optical limiting devices for protection of human eyes against laser.

Summary:

Fullerenes possess optical limiting properties due to reverse saturable absorption (RSA). But the low solubility, thermal instability and tendency to form clusters have restricted the direct applications of fullerenes. In contrast, fullerenes, after functionalized, can be easily mixed with silica gel, via sol-gel route.

The silica-C_{60} hybrids were stable under continuous attack of strong laser pulses and it was observed that even then optical limiting power of these hybrids was retained

Non-linear absorption of the product shows the OL effect due to C_{60}, and is related to the concentration of C_{60} in the matrix.

These hybrid materials may have applications in areas such as optical devices, semiconductors, chemical sensors, catalysis and in the medical field.

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