

## Properties of Fullerene as Photosensitizer and its Catalytic Application: Review

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**Abstract:** Under irradiation, the semiconductor is excited to generate hole and electron pairs, and the holes subsequently react with adsorbed hydroxyl ions to generate hydroxyl radicals, while the electrons react with adsorbed oxygen to generate superoxide ions. These oxidizing substances, which have higher reaction activity than common oxygen molecules, can completely destroy various organic pollutants in wastewaters. In order to enhance the photochemically generated oxygen species efficiency and to search for new highly active photocatalysts, it is necessary to study new catalysts. Titania (TiO<sub>2</sub>) as photocatalyst has been used for the past few decades in a wide range of applications. The most common application is the purification of air and water by removing toxic compounds. There is limited use since the efficiency is not high enough and its utilization remains typically confined to UV light. Two problems that need to be addressed with nanosize photocatalysts is the difficulty in distribution single particles and collecting them after use. Additionally, C<sub>60</sub> is one of the most promising materials for this application because of its band gap energy, which is about 1.6–1.9 eV. It has strong absorption in the ultraviolet region and weak but significant bands in the visible region. In general, coupled systems exhibit higher degradation rates as well as an increased extent of degradation different dyes. They were combined with metal chalcogenide to form a composite material.

**Keywords :** fullerene, photosensitizer, catalytic activity, Titania

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### 1. Introduction

Bioaerosols [1], consist of viruses [2], bacteria cellular fragments [3], fungal spores and by-products of microbial metabolism [4], can be presented as particulates [5], liquid or volatile organic compounds [6]. Previous studies documented that bioaerosols could be responsible for allergic responses [7], infectious diseases [8], respiratory problem (asthma for example) and hypersensitivity reactions [9]. There are various techniques to mitigate the problem of biological contamination in the indoor environment [10], including purging with outdoor air [11], filtering microbiological species [12], isolating through pressurization

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control [13], using ultraviolet germicidal irradiation (UVGI) and ozone [14], chemical oxidation. However, different techniques have different limitations. Ventilation can only dilute the concentration in the air stream but cannot remove or destroy biological species. Moreover, the impact to the energy consumption can be huge for purging large amount of outdoor air into the indoor environment [15]. Filtration cannot permanently remove the contaminants, and some microbes may not be easily filtered. Ultraviolet disinfection has the limitation in low throughputs, high energy consumption and the unavailability of intensive lamps with a wavelength of lower than 254 nm [16]. Ozone is extremely reactive and a trace amount of ozone is hazardous to human [17].

The mechanisms of the PCO antimicrobial process have been studied and several complex reaction pathways have been reported [18]. The first proposed killing mechanism implies an oxidation of the intracellular coenzyme A (CoA), which inhibits cell respiration and subsequently causes cell death as a result of a direct contact between  $\text{TiO}_2$  and target cell, leading to cell death [19]. The fundamentals of photophysics and photochemistry underlying the heterogeneous photocatalysis employing the semiconductor  $\text{TiO}_2$  catalyst have been intensively reported in many literatures [20].

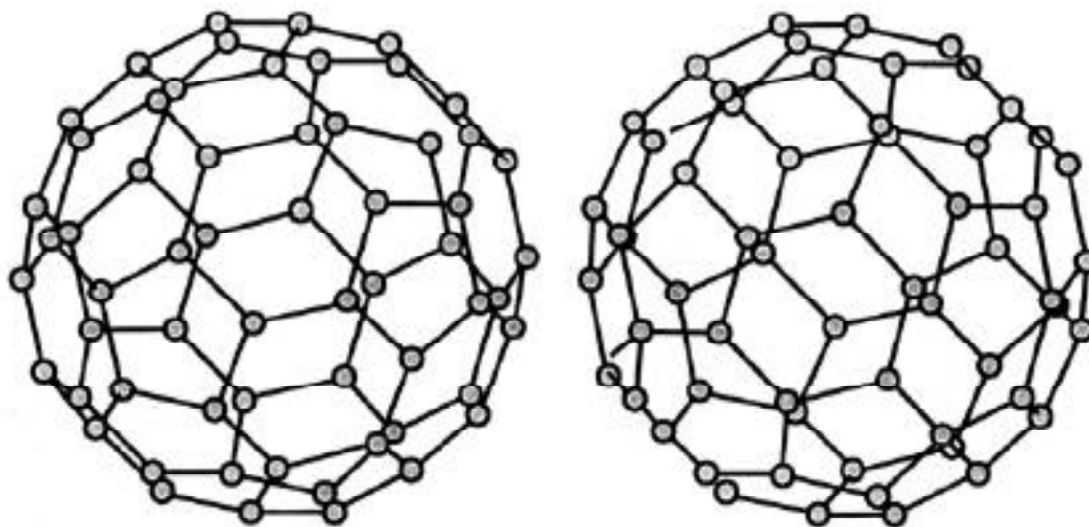
Vinodgopal and Kamat (1992) reported the dependence of the photodegradation rate of the organic surrogate on surface coverage of the photocatalysts used [21]. Although  $\text{H}_2\text{O}_2$  may be generated via the  $\text{TiO}_2$  photocatalysis, its relative amount in the system may be inadequate to drive the Fenton reaction. Many researchers have reported the addition of  $\text{H}_2\text{O}_2$  in enhancing both the photo-Fenton and  $\text{TiO}_2$  photocatalysis reactions [22]. Recombination of photogenerated charge carriers is the major limitation in semiconductor photocatalysis as it reduces the overall quantum efficiency [23]. When recombination occurs, the excited electron reverts to the valence band without reacting with adsorbed species [24] non-radiatively or radiatively, dissipating the energy as light or heat [25]. Binary catalysts with silica or zirconia and  $\text{TiO}_2$  were also shown to have significantly higher activities than pure titania for the complete photocatalytic oxidation of ethylene [26]. This may be due to  $\text{TiO}_2/\text{SiO}_2$  and  $\text{TiO}_2/\text{ZrO}_2$  having a higher surface acidity [27]. However, isoelectric point measurements employing the sintered and unsintered catalysts showed no conclusive increase in surface acidity [28]. The mechanism of this promotion effect is not yet clearly understood. Mendez-Roman and Cardona-Martinez (1998) found the  $\text{SiO}_2\text{-TiO}_2$  photocatalyst more active than  $\text{TiO}_2$  and also that it deactivates at a slower rate. The binary oxide also seemed to have a higher toluene adsorption capacity than  $\text{TiO}_2$ . Some reports in the literature have shown that the incorporation of lanthanide ions such as  $\text{La}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ , and  $\text{Sm}^{3+}$  into the  $\text{TiO}_2$  matrix could promote the chemical or physical adsorption of organic substrates on the catalyst's surface [29].

[60]-Fullerenes are widely known because of their unique electronic properties [30]. They are well established as singlet oxygen sensitizers in the context of organic synthesis photooxidations [31], in electron donor-acceptor assemblies as part of artificial photosynthetic systems [32] and in photochemical solar cells [33], to mention just a few examples. However, their application in  $\text{TiO}_2$  photocatalysis is much less well explored, with only a few handfuls of studies readily available in the published literature.

The basis for the enhancement of  $\text{TiO}_2$  photocatalysis by [60]-fullerenes is well summarised by Apostolopoulou et al. [34]: [60]-fullerene absorbs moderately in the visible and strongly in the UV region of the spectrum [35]. Under UV/visible irradiation, it undergoes excitation from its ground state to a transient ( $\sim 1.2$  ns [36] singlet excited state ( ${}^1\text{C}_{60}^*$ ), which then goes through rapid intersystem crossing (at a rate of  $5.0 \times 10^{-8} \text{ s}^{-1}$ ) to a longer lasting ( $>40 \mu\text{s}$ ) lower lying triplet state ( ${}^3\text{C}_{60}^*$ ) [37]. Of primary significance is that fullerenes in their excited states are both better electron donors and better electron acceptors than in their ground state (capable of accepting as many as six electrons [38]).

## 2. Origins of fullerenes

Carbon has been thoroughly studied and its properties known and documented for many years. Readily combining with many different elements, carbon is found in innumerable simple and complex molecular compounds. Previous to 1985, however, pure carbon was thought to exist in only two naturally occurring, solid forms: diamond and graphite. This all changed in 1985 and scientists were forced to alter their perception of the natural world with the discovery of a third allotropic form of solid carbon, the buckminsterfullerene [39]. Buckminsterfullerenes, or the more affectionately named, "buckyball," are symmetrical, ball-shaped molecules consisting of sixty carbon atoms arranged in an icosahedral geometric structure resembling a soccer ball. Fig. 1 illustrates the icosahedral symmetry of the buckminster fullerene molecule. Buckminsterfullerenes are so named because of their resemblance to the geodesic dome structures created by famed architect R. Buckminster Fuller. (Harris, 1999).



Stereographic projection of  $\text{C}_{60}$ . To visualize the 3D image the picture must be held about 15 cm from the eyes and the eyes must focus at infinity.

**Figure 1:** 3D Visualization of the Buckminster Fullerene Molecule (Dresselhaus, 1996) [39]

Buckyballs were discovered by accident in August of 1985 at Rice University in Houston Texas by Richard Smalley and Harry Kroto. Smalley, a professor and researcher at Rice, was working on the study of laser vaporization and its application in synthesizing clusters of semiconducting materials such as Silicon and Gallium Arsenide. Kroto, a University of Sussex professor was visiting Rice in hopes of recreating, in the laboratory, processes that take place on the surface of Red Giant stars. Together, with the assistance of a team of graduate students, Kroto and Smalley vaporized clusters of carbon atoms from a graphite substrate using a high powered laser. Employing a mass spectrometer to measure carbon clusters in the condensing plasma, the team discovered, quite unexpectedly, that clusters of  $C_{60}$  occurred repeatedly in large quantities [40]. A graph of the mass spectrometer reading is included in Fig. 2.

After developing a number of hypotheses in regards to the geometry of the newly discovered molecule, Kroto and Smalley agreed on a conceptual structure resembling a symmetrical, closed cluster where the carbon atoms are bonded to each other in a spheroidal molecule of great stability. The two researchers published their findings in November of 1985 in the journal *Nature*. (Harris, 1999) Kroto and Smalley later shared the 1996 Nobel Prize for Chemistry with Robert Curt of Rice University for their discovery of the buckminsterfullerene. (Browne, 1998).

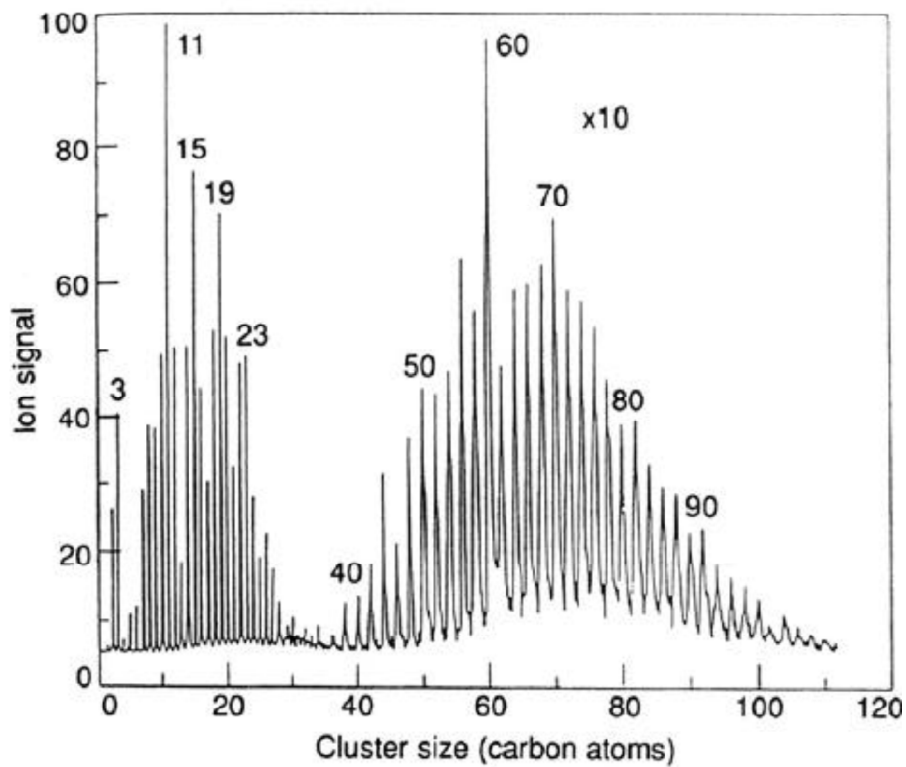


Figure 2: Mass spectrometry data illustrating the preponderance of  $C_{60}$ . (Dresselhaus, 1996) [41]

After the momentous discovery, the next step in the ultimate quest to produce commercial applications for this new form of carbon was to develop a method to produce large quantities of fullerenes [41]. Originally, only minute amounts of buckyballs could be produced using the laser vaporization methods established by Smalley and Kroto. The breakthrough came from yet another duo of scientists, Wolfgang Krätschmer of the Max Planck Institute at Heidelberg and Donald Huffman of the University of Arizona. The two researchers and their associates used a carbon arc to vaporize graphite in a helium atmosphere, thus producing fullerene rich soot particles. Dissolving the soot in benzene produced a red solution containing fullerene crystals (90% C<sub>60</sub> and 10% C<sub>70</sub>) [42]. Using this improved method, large quantities of pure fullerene crystals could be precipitated out of the benzene solution after drying [43].

### 3. Description

Fullerenes (first discovered in 1985 by Robert Curl, Harold Kroto, and Richard Smalley), are a class of hollow, spherical, or ellipsoid molecules – composed entirely of carbon atoms – in a cage-like structure composed of pentagonal and hexagonal faces. They were named after the architect Richard Buckminster Fuller due to their similarity to his geodesic dome design, and are often referred to as “buckyballs”. Fullerenes were the seventh allotropic form of carbon to be discovered (together with the two forms of diamond, the two forms of graphite, chaoit, and carbon (IV)). Their discovery led to Curl, Kroto, and Smalley receiving the Nobel Prize for Chemistry in 1996. Fig. 3 provides a graphical representation of the 60-carbon atom containing C-60 fullerene, and Fig. 4 illustrates a graphical representation of the 540-carbon atom containing C-540 fullerene.

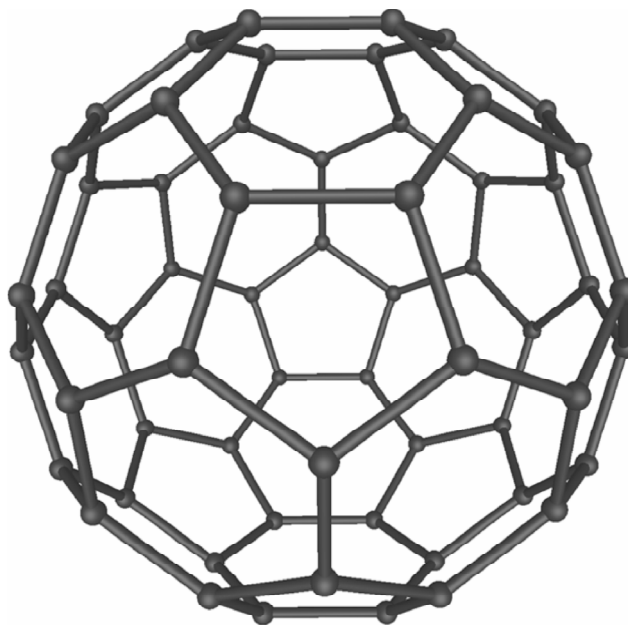


Figure 3.3: C-60 fullerene [43]

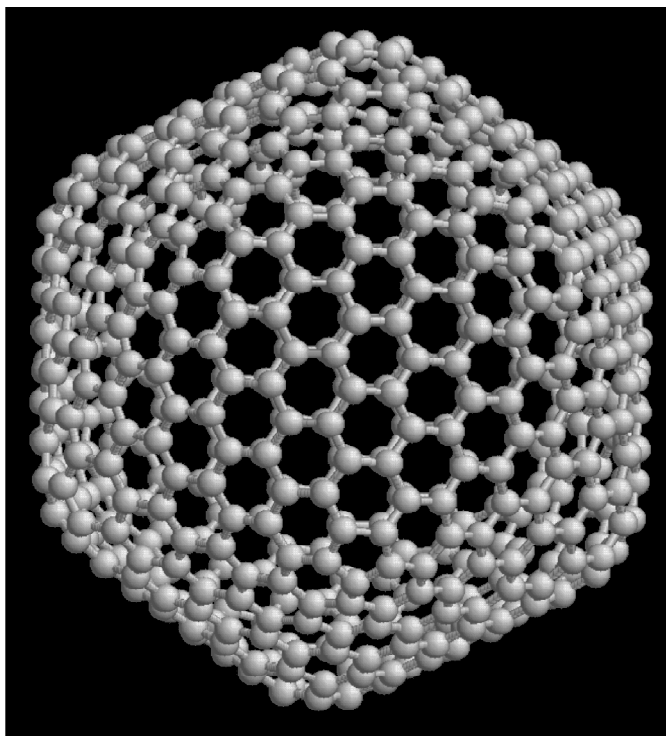


Figure 3.4: C-540 fullerene [44]

An infinite number of spherical fullerenes are believed to be able to exist. Known forms include C-60, C-70, C-76, C-84, C-240, and C-540 (Fig. 5). All fullerenes consist of 12 pentagonal faces and a varying number of hexagonal faces. In general, for a fullerene C- $n$  there will be 12 pentagonal faces and half of  $n$  minus 10 ( $n/2-10$ ) hexagonal faces; thus, the C-60 fullerene has 12 pentagonal faces and 20 hexagonal faces [44].

Fullerenes have a rich and complex chemistry (Stevens 1994, Kadish and Roff 2000, Taylor 1995, Andreoni 2000, Hirsch *et al.* 2005) that led to the publication of over 15,000 academic papers within 15 years of their discovery. C-60 behaves like an electron deficient alkene, reacts readily with electron rich species, and participates in many reactions (including oxidations, reductions, nucleophilic additions, electrophilic additions, Diels-Alder reactions, and Friedel-Craft alkylations). This rich chemistry permits a wide range of fullerene functionalization and opens the way to designing functionalized fullerene for specific properties and purposes.

A large number of applications have been suggested for basic fullerenes and their functionalized derivatives. Potential applications include organic photovoltaics, polymer electronics, antioxidants, biopharmaceuticals, antibacterials, HIV inhibition, catalysts, water purification, MRI agents, optical devices, scanning tunneling microscopy, and atomic force microscopy [45]. Fullerenes have also been the subject of many studies related to radioactive materials. They are being extensively investigated as carrier species for medical

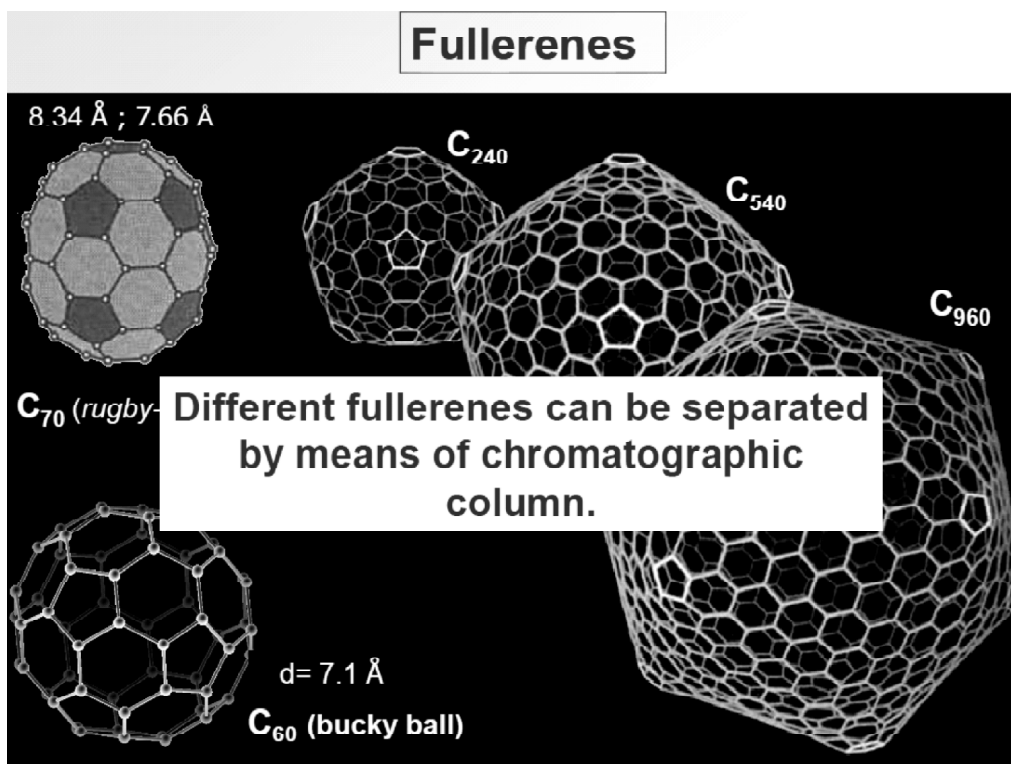
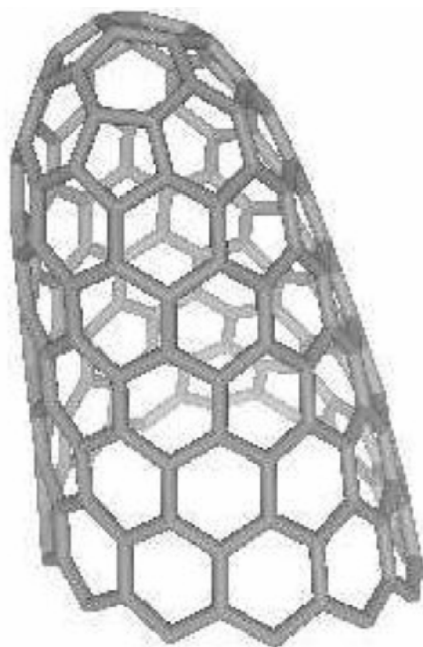


Figure 5: Different fullerenes can be separated by means of chromatographic column [45]

radionuclides in cancer therapy. It has been observed that in the combustion of coal, which contains small amounts of uranium, nanocrystals of the mineral uraninite are encased in fullerene-type cages. This potentially provides an unanticipated pathway for radiation exposure [46]. They have also been explored as a technology for radioactive waste management. DOE has determined that there are three major isotopes contributing to public radiation dose as a consequence of radionuclide releases – iodine-129, technetium-99, and neptunium-237 – and fullerenes have been investigated as a sorbent for iodine. It is also worth noting that a structure closely related to fullerenes, the carbon nanohorn (Fig. 6), has been suggested as a possibility for radioactive waste disposal.

#### 4. Production methods

Fullerenes are in fact produced in small amounts naturally, in fires and lightning strikes, and there is some evidence that the massive Permian extinction of 250 million years ago was caused by the impact of an object containing buckyballs. However, they were first produced by man (at least knowingly) in the soot resulting from vaporizing graphite with a laser [47]. The earliest bulk production process is the arc discharge (or Krätschmer-Huffman) method, using graphite electrodes, developed in 1990. This produces predominantly  $C_{60}$  and  $C_{70}$  but can be made to produce higher fullerenes, for instance by having more porous electrodes. Separation with solvents such as toluene can achieve



**Figure 6:** The carbon nanohorn [47]

near 100% purity for  $C_{60}$ . A little later, a group at MIT started producing  $C_{60}$  in a benzene flame. And pyrolysis (transformation of a compound by heat, without burning) of a variety of aromatic compounds has also been used to produce fullerenes (aromatic compounds have benzene-derived ring structures. A typical attribute of aromatics is that they have bonding electrons free to move around, so-called delocalized electrons. Fullerenes themselves are aromatic).

Methods such as sputtering and electron beam evaporation (with a graphite precursor) have been shown to preferentially produce higher fullerenes, such as  $C_{70}$ ,  $C_{76}$ ,  $C_{78}$ , and  $C_{84}$ . UCLA has patents on these approaches [48].

## 5. Characterization of fullerene

The peak at around  $1000\text{ cm}^{-1}$  is assigned to C–O–C and at  $1600\text{ cm}^{-1}$  to C=O. Both peaks are similar to those in the prolonged ozonation product of fullerene in a solution. FT-IR spectra of pristine  $C_{60}$  powder show sharp absorption characteristic peaks of  $C_{60}$  ( $526$ ,  $576$ ,  $1184$ , and  $1429\text{ cm}^{-1}$ ), indicating that the specimens were composed of fullerene  $C_{60}$  molecule.

The X-ray diffraction pattern, shown in Fig. 8 is for  $C_{60}$  in its crystalline structure [49]. The most important XRD feature which provides a proof for existence of the cells is the observation of diffraction peaks due to  $0\ 0\ 2$  planes. This is the most prominent peak in Fig. 3.8 while diffractions from  $0\ 0\ 6$ ,  $3\ 0\ 0$ , and  $1\ 1\ 4$  planes are appeared in smaller intensities. Peak  $1\ 1\ 2$ ,  $1\ 1\ 0$ , and  $0\ 0\ 2$  is appeared in its characteristic region  $2\theta = 4.3$ ,  $5.1$  and  $8.5$  as a broad peak. Other detectable peaks are  $0\ 0\ 4$ ,  $1\ 0\ 1$  and  $1\ 0\ 0$ .



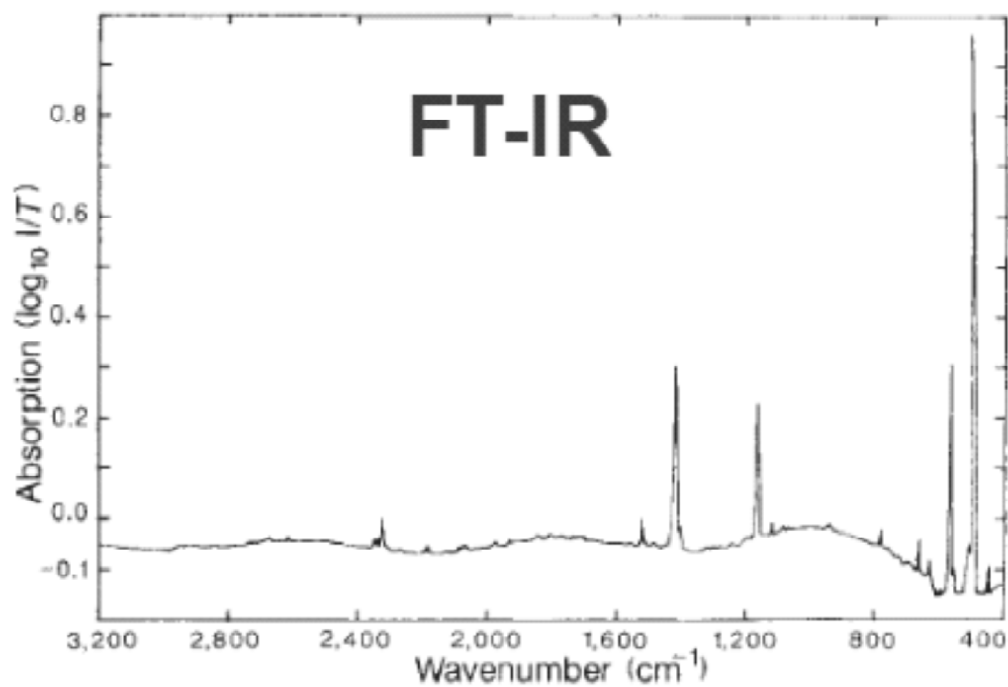


Figure 7: FT-IR spectra of pristine C<sub>60</sub> powder [49].

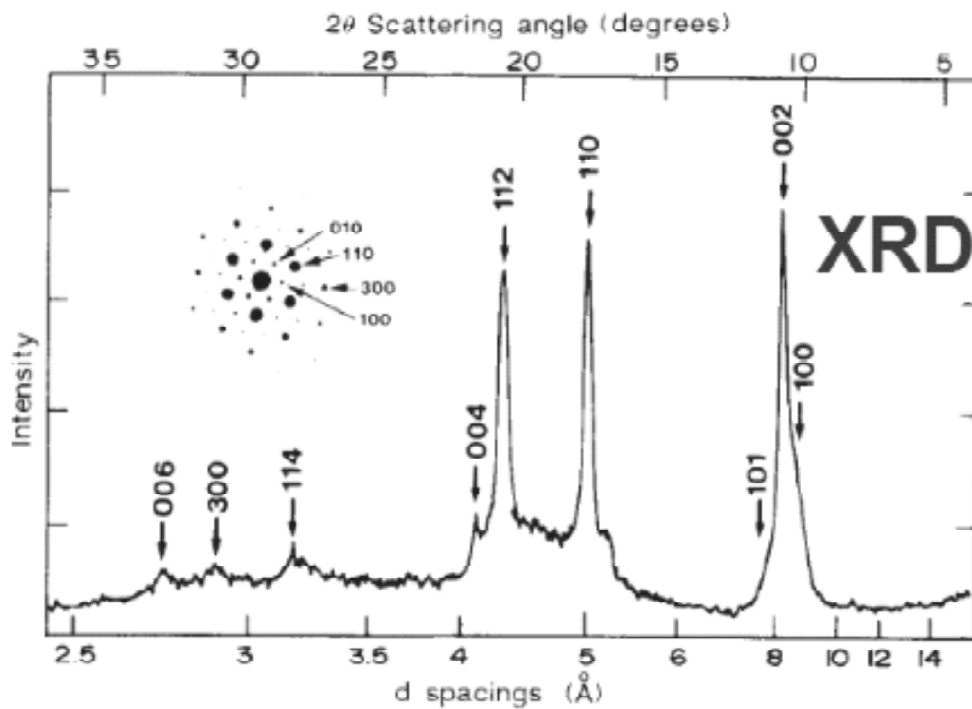


Figure 8: XRD for fullerene [49].

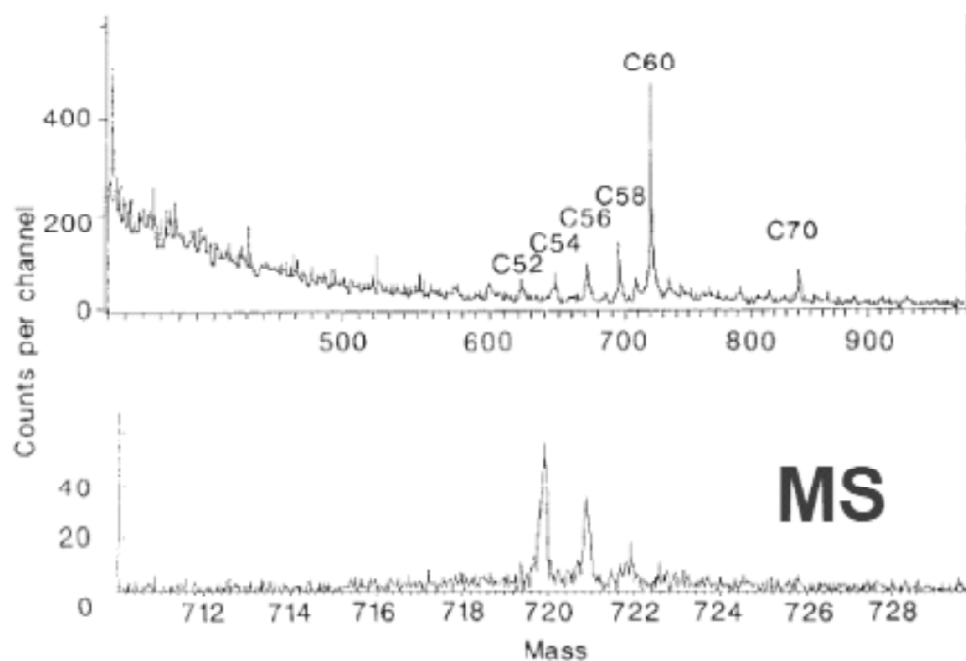


Figure 9: Typical negative-ion ESI FT-ICR mass spectrum of a fullerene sample [4].

Fig. 9 shows a typical negative-ion ESI FT-ICR mass spectrum of a fullerene sample. Assignment of the mass peaks in Fig. 1 is achieved by contrasting the isotope distribution

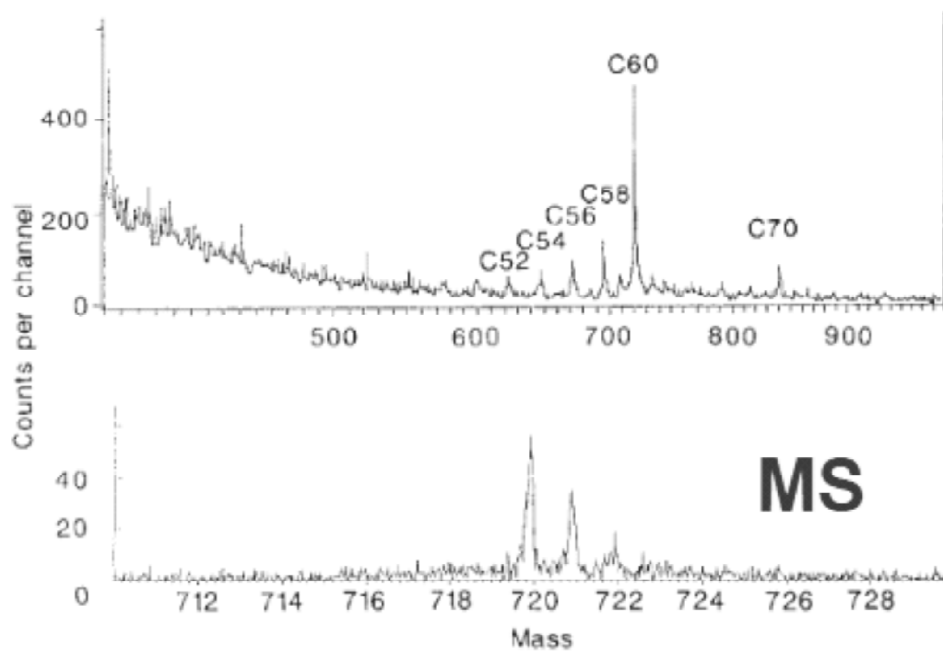
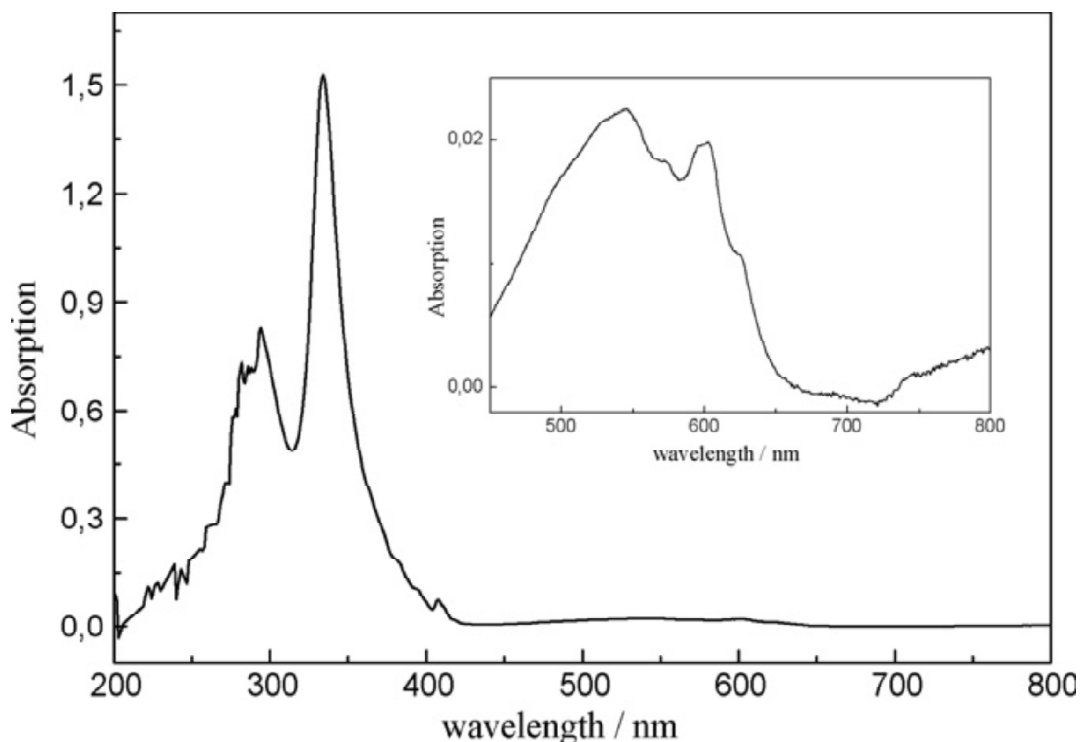


Figure 10: Raman spectra of  $C_{60}$  and  $C_{70}$  [48].

(based on the natural abundances of  $^{12}\text{C}$  and  $^{13}\text{C}$ ) of the measured spectrum with the calculated distribution. Fullerene isotopomers are spaced by 1 and 0.5 Dalton for singly and doubly charged ions, respectively. In ICR mass spectrometry care has to be taken to distinguish the dianion signal from second harmonics of the signal at the fundamental ICR orbital frequencies. This was accomplished by: (i) isolating the dianions in the Penning trap from the singly charged ions by means of resonant RF excitation and (ii) by observing the frequency shift upon varying the DC trapping voltage [4]. We were therefore able to assign mass peaks unequivocally as follows.

Figure 5 compares the Raman spectra of  $\text{C}_{60}$  and  $\text{C}_{70}$ . The main feature in the  $\text{C}_{60}$  spectrum is a relatively sharp line at around  $1462\text{ cm}^{-1}$ , known as the pentagonal pinch mode. This tells us several things. Firstly, it tells us that  $\text{C}_{60}$  is composed of  $\text{sp}^2$  bonded carbon. The sharpness of the band also tells us that the bonds are for the most part very uniform in nature. In fact, the carbon atoms in  $\text{C}_{60}$  are equivalent and indistinguishable. In contrast, the spectrum of  $\text{C}_{70}$  is littered with numerous bands. This is due to a reduction in molecular symmetry which results in more Raman bands being active. Additionally Raman can also be very sensitive to doping and stress due to temperature or pressure.

Fig. 11 illustrates the electronic spectrum of the  $\text{C}_{60}$  molecules in a solution of 1,2-dichlorobenzene. Two strong absorption peaks in the ultraviolet (284, 335 nm), a smaller



**Figure 11:** Absorption spectrum of a  $\text{C}_{60}$  solution in 1, 2 dichlorobenzene recorded at room temperature in the range 200–800 nm [48].

absorption peak at 408nm and a very weak band extended in the visible region appear in the UV-vis absorption spectrum of the dissolved  $C_{60}$ . Magnification of the spectrum in the visible region shows that the wide band (475–650 nm) is rather structured involving five peaks at about 460, 525, 550, 600 and 625 nm.

## 6. Properties of fullerenes

Physically, buckyballs are extremely strong molecules, able to resist great pressure – they will bounce back to their original shape after being subjected to over 3,000 atmospheres. Their physical strength does seem to offer potential in materials. However, like nanotubes, they do not bond to each other chemically, sticking together instead through much weaker forces – van der Waals – the same forces that hold layers of graphite together. This gives buckyballs, like graphite, potential as a lubricant, though the molecules tend to be too small for many applications, getting stuck in crevices. Buckyballs with shells around them, known as nano-onions, or bucky-onions, are larger and potentially better as a lubricant [50]. A technique for creating these with quite high purity using an underwater arc approach was demonstrated in December 2001 by a group from the University of Cambridge in the UK and the Himeji Institute of Technology in Japan.

Although buckyballs do not stick together well, this does not mean they do not have applications in solids. When incorporated in relatively low amounts in a polymer matrix they can be held in place and impart some of their strength and low density to the material. Companies such as BuckyUSA are working with the tire industry to establish whether  $C_{70}$  would be a superior additive to carbon black [51].

Research has been done on making buckyballs less slippery. Shortly before the aforementioned production of nano-onions, Lars Hultman and colleagues, of the University of Linköping in Sweden, replaced some of the carbon atoms in buckyballs with nitrogen atoms, allowing them to bond, producing a material that is hard but elastic. These modified buckyballs also formed shells and were also called nano-onions.

Fullerenes and related substances have shown considerable potential as catalysts (basically, substances that enhance a reaction without being consumed themselves). A team at the Fritz Haber Institute in Berlin has used bucky-onions to convert ethylbenzene into styrene, one of the ten most important industrial chemical processes. Existing approaches are limited to a maximum yield of 50% but the researchers achieved styrene yields of 62% in preliminary experiments, and expect further improvement. The bucky-onions seem, however, to be a precursor to the catalyst as they were converted in the reaction into a material that had lost the regular, was an effective catalyst [52].

SRI International have also been looking at the catalytic properties of fullerenes and related materials, including the soot produced alongside the fullerenes using arc or combustion methods. This soot contains a variety of carbon forms that can be partially like fullerenes (composed of hexagons and pentagons) but probably with open areas that serve as catalytic sites. The soot can be used for hydrogenation/dehydrogenation of aromatics, for upgrading of heavy oils, and for conversion of methane into higher hydrocarbons by pyrolytic or reforming processes.

Fullerenes have interesting electrical properties, which have led to suggestions of use in a number of electronics-related areas, from data storage devices to solar cells. Researchers at Virginia Tech have used ultra-thin layers of fullerenes as electron acceptors in flexible organic solar cells. Currently the efficiency is about a fifth of conventional silicon photovoltaics (so about 3-4%, compared to 15-20% for mass market silicon solar cells) but the researchers expect to be able, through better control of the nanostructure, to equal or exceed the efficiency of current silicon-based devices. The same properties also offer potential use in photodetectors for X-rays. Work by Siemens on this is discussed later.

Another use of the electrical properties of fullerenes is in fuel cells. Sony has used them to replace large polymer molecules in the electrolytic membrane of direct methanol fuel cells (with personal electronics being the intended application). The result is a fuel cell capable of operating at lower temperatures than those with polymer-only membranes, and Sony believes the fullerene-based membranes might even work out cheaper. Sony have also been using fullerenes in work on hydrogen-based fuel cells, exploiting their ability to help move protons around (proton exchange membranes are the basis of such fuel cells). Fullerenes have been inserted into nanotubes, the result sometimes being referred to as 'peapods'. The earliest work on this was done early in 2002 in South Korea (Seoul National University) and the US (University of Pennsylvania in Philadelphia), using  $C_{82}$  and  $C_{60}$  respectively. The fullerenes alter the electrical behavior of the nanotubes, creating regions of varying semiconducting properties, effectively producing a series of tiny transistors within a nanotube. The properties can be modified by moving the location of the enclosed fullerenes and researchers at Michigan State University have even suggested using this to create memory devices. Such work is still at the very early research stage and applications should not be expected any time soon, if ever (there are many competing approaches to nanoelectronics and memory).

## 7. Conclusion

Considerable interest was generated in the second half of 2001 by research at Lucent's Bell Labs that showed that buckyballs could be made superconducting at above the temperature of liquid nitrogen, a very important find because liquid nitrogen is relatively cheap to produce but lower temperatures are much harder to maintain. However, some work on molecular electronics by the same researcher, Hendrik Schön, was called into question because of identical graphs being used in different papers to represent different results. Later the buckyball work was similarly questioned and indeed his results have not been duplicated by other researchers. Fullerenes and their derivatives have indeed been shown to be superconducting, but only at very low temperatures (a few tens of degrees centigrade above absolute zero). Around the same time there was also a claim that a polymer had been created out of buckyballs that was magnetic at room temperature, making the first non-metallic magnetic material. Though no wrong-doing has been suggested in this case, these results also have not been reproduced. Besides which, in terms of potential value, this result was trumped shortly afterwards by the creation of a polymer (without buckyballs) that was also shown to be magnetic at room temperature,

and considerably more so. Fullerenes can also be used as precursors for other materials, such as diamond coatings or nanotubes (Sony, for example, creates nanotubes by heating fullerenes and platinum). On the esoteric side, fullerenes have been used in fundamental research in quantum mechanics, being the largest particles in which the wave/particle duality of matter has been demonstrated, by getting a  $C_{60}$  molecule to appear to pass through two different slits simultaneously, a famous experiment normally performed with electrons, photons or single atoms.

### Reference

- [1] K. Rajeshwar, M.E. Osugi, W. Chanmanee, C.R. Chenthamarakshan, M.V.B. Zanoni, P. Kajitvichyanukul, R. Krishnan-Ayer, Heterogeneous photocatalytic treatment of organic dyes in air and aqueous media, *J. Photochem. Photobiol. C: Photochem. Rev.* 9 (2008) 171-192.
- [2] H. Zhang, G. Chen, D.W. Bahnemann, Photoelectrocatalytic materials for environmental applications, *J. Mat. Chem.* 19 (2009) 5089-5121.
- [3] M.D. Hernández-Alonso, F. Fresno, S. Suárez, J.M. Coronado, Development of alternative photocatalysts to TiO<sub>2</sub>: challenges and opportunities, *Energy Environ. Sci.* 2 (2009) 1231-1257.
- [4] R. Vinu, G. Madras, Environmental remediation by photocatalysis, *J. Indian Inst. Sci.* 90 (2010) 189-230.
- [5] T.K. Tseng, Y.S. Lin, Y.J. Chen, H. Chu, A review of photocatalysts prepared by sol-gel method for VOCs removal, *Int. J. Mol. Sci.* 11 (2010) 2336-2361.
- [6] J.H. Kou, J. Gao, Z.S. Li, Z.G. Zou, Research on photocatalytic degradation properties of organics with different new photocatalysts, *Curr. Org. Chem.* 14 (2010) 728-744.
- [7] D. Zhang, G. Li, J.C. Yu, Inorganic materials for photocatalytic water disinfection, *J. Mater. Chem.* 20 (2010) 4529-4536.
- [8] J. Matos, J. Laine, J.-M. Herrmann, Synergy effect in the photocatalytic degradation of phenol on a suspended mixture of titania and activated carbon, *Appl. Catal. B: Environ.* 18 (1998) 281-291.
- [9] J. Matos, J. Laine, J.-M. Herrmann, Effect of the type of activated carbons on the photocatalytic degradation of aqueous organic pollutants by UV-irradiated titania, *J. Catal.* 200 (2001) 10-20.
- [10] J. Araña, J.M. Doña-Rodríguez, E. Tello Rendón, C. Garriga i Cabo, O. González- Díaz, J.A. Herrera-Melián, J. Pérez-Peña, G. Colón, J.A. Navío, TiO<sub>2</sub> activation by using activated carbon as a support. Part II. Photoreactivity and FTIR study, *Appl. Catal. B: Environ.* 44 (2003) 153-160.
- [11] J. Matos, J. Laine, J.-M. Herrmann, D. Uzcategui, J.L. Brito, Influence of activated carbon upon titania on aqueous photocatalytic consecutive runs of phenol photodegradation, *Appl. Catal. B: Environ.* 70 (2007) 461-469.
- [12] J. Matos, E. García-López, L. Palmisano, A. García, G. Marci, Influence of activated carbon in TiO<sub>2</sub> and ZnO mediated photo-assisted degradation of 2-propanol in gas-solid regime, *Appl. Catal. B: Environ.* 99 (2010) 170-180.
- [13] M. Inagaki, F. Kojin, B. Tryba, M. Toyoda, Carbon-coated anatase: the role of the carbon layer for photocatalytic performance, *Carbon* 43 (2005) 1652-1659.
- [14] T. Tsumura, N. Kojitani, I. Izumi, N. Iwashita, M. Toyoda, M. Inagaki, Carbon coating of anatase type TiO<sub>2</sub> and photoactivity, *J. Mater. Chem.* 12 (2002) 1391-1396. [16] B.
- [15] Tryba, A.W. Morawski, T. Tsumura, M. Toyoda, M. Inagaki, Hybridization of adsorptivity with photocatalytic activity - carbon-coated anatase, *J. Photochem. Photobiol. A: Chem.* 167 (2004) 127-135.
- [16] Kitano M, Tsujimaru K, Anpo M. Hydrogen production using highly active titanium oxide-based photocatalysts. *Top Catal* 2008; 49(1): 4-17.
- [17] Osterloh FE. Inorganic materials as catalysts for photochemical splitting of water. *Chem Matter* 2007; 20(1): 35-54.

- [18] H. Fu, L. Zhang, S. Zhang, Y. Zhu, J. Zhao, Electron spin resonance spintrapping detection of radical intermediates in N-doped TiO<sub>2</sub>-assisted photodegradation of 4-chlorophenol, *J. Phys. Chem. B* 110 (2006) 3061–3065.
- [19] H. Hsu, S. Chen, Y. Chen, Removal of chromium(VI) and naphthalenesulfonate from textile wastewater by photocatalysis combining ionic exchange membrane processes, *Sep. Purif. Technol.* 80 (2011) 663–669.
- [20] P.R. Shukla, S. Wang, H.M. Ang, M.O. Tade, Photocatalytic oxidation of phenolic compounds using zinc oxide and sulphate radicals under artificial solar light, *Sep. Purif. Technol.* 70 (2010) 338–344.
- [21] C. Hsieh, W. Fan, W. Chen, J. Lin, Adsorption and visible-light-derived photocatalytic kinetics of organic dye on co-doped Titania nanotubes prepared by hydrothermal synthesis, *Sep. Purif. Technol.* 67 (2009) 312–318.
- [22] Cho, M., Yoon, J., 2008. Measurement of OH radical CT for inactivating *Cryptosporidium parvum* using photo/ferrioxalate and photo/TiO<sub>2</sub> systems. *J. Appl. Microbiol.* 104, 759-766.
- [23] W. Choi, A. Termin, M.R. Hoffmann, The role of metal ion dopants in quantum-sized TiO<sub>2</sub>: Correlation between photoreactivity and charge carrier recombination dynamics, *Journal of Physical Chemistry B* 98 (1994) 13669–13679.
- [24] A. Sclafani, Comparison of the Photoelectronic and Photocatalytic Activities of Various Anatase and Rutile Forms of Titania in Pure Liquid Organic Phases and in Aqueous Solutions, *Journal of Physical Chemistry* 100 (1996) 13655–13661.
- [25] J. Liqiang, Q. Yichun, W. Baiqi, L. Shudan, J. Baojiang, Y. Libin, F. Wei, F. Honggang, S. Jiazhong, Review of photoluminescence performance of nano-sized semiconductor materials and its relationships with photocatalytic activity, *Solar Energy Materials & Solar Cells* 90 (2006) 1773–1787.
- [26] K. Vinodgopal, P.V. Kamat, *Environmental Science and Technology* (1995) 29.
- [27] Z.L. Xu, J. Shang, C.M. Liu, C. Kang, H.C. Guo, Y.G. Du, *Materials Science and Engineering B* (1999) 63.
- [28] Herrmann, J.M., Disdier, J., Pichat, P., 1988. Photocatalytic deposition of silver on powder titania: consequences for the recovery of silver. *J. Catal.* 113, 72-81. [1] M.R. Hoffmann, S.T. Martin, W.Y. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, *Chem. Rev.* 95 (1995) 69–96.
- [29] Herrmann, J.M., 1999. Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catal. Today* 53, 115-129.
- [30] Makarova T. Electrical and optical properties of pristine and polymerized fullerenes, *Semiconductors* 2001;35(3):243–78.
- [31] Arbogast JW, Darmanyan AP, Foote CS, Diederich FN, Whetten RL, Rubin Y, *et al.* Photophysical properties of sixty atom carbon molecule (C<sub>60</sub>), *J Phys Chem* 1991; 95(1): 11–2.
- [32] Fuzumi S. Development of bioinspired artificial photosynthetic systems, *Phys Chem Chem Phys* 2008; 10: 2283–97.
- [33] D'Souza F, Ito O. Supramolecular donor-acceptor hybrids of porphyrins/phthalocyanines with fullerenes/carbon nanotubes: electron transfer, sensing, switching, and catalytic applications, *Chem Commun* 2009(33): 4913–28.
- [34] Po R, Maggini M, Camaioni N. Polymer solar cells: recent approaches and achievements, *J Phys Chem C* 2009; 114(2): 695–706.
- [35] Apostolopoulou V, Vakros J, Kordulis C, Lycourghiotis A. Preparation and characterization of [60] fullerene nanoparticles supported on titania used as a photocatalyst, *Colloids Surf A* 2009; 349(1–3): 189–94.
- [36] Krätschmer W, Fostiropoulos K, Huffman DR. The infrared and ultraviolet absorption spectra of laboratory-produced carbon dust: evidence for the presence of the C<sub>60</sub> molecule, *Chem Phys Lett* 1990; 170(2–3): 167–70.

- [37] Ebbesen TW, Tanigaki K, Kuroshima S. Excited-state properties of C60. *Chem Phys Lett* 1991; 181(6): 501-4.
- [38] Xie Q, Perez-Cordero E, Echegoyen L. Electrochemical detection of C60- and C70-: enhanced stability of fullerenes in solution. *J Am Chem Soc* 1992; 114(10): 3978-80.
- [39] Andreoni, W. (Ed.). 2000. *The Physics of Fullerene-Based and Fullerene-Related Materials*. Kluwer Academic Publishers, The Netherlands.
- [40] Barrera, E.V., J. Sims, D.L. Callahan, V. Provenzano, J. Milliken, R.L. Holtz. 1994. Processing of fullerene-reinforced composites. *Journal of Materials Resources*. 9(10): 2662-2669.
- [41] Investigation of photoexcitations of conjugated polymer/fullerene composites embedded in conventional polymers. *Journal of Chemical Physics*. 109(3): 1185-1195, 1998.
- [42] Cabio'h, T., J.P. Riviere and J. Delafond. 2005. A new technique for fullerene anion formation. *Journal of Materials Science*. 30(19): 4787-4792.
- [43] Calleja, F.J., L. Giri, T. Asano, Ti. Mieno, A. Sakurai, M. Ohnuma, and C. Sawatari. 1996. Structure and mechanical properties of polyethylene-fullerene composites. *Journal of Materials Science*. 31(19): 5153-5157.
- [44] Fu, X., D. Wu, X. Zhou, H. Shi, Z. Hu. 2005. Solvothermal synthesis of molybdenum disulfide hollow spheres modified by Cyanex 301 in water-ethanol medium. *Journal of Nanoparticle Research*. 9(4): 675-681.
- [45] Golberg, D. Y. Bando, K. Kurashima, T. Sasaki. 1999. Fullerene and anion formation under electron irradiation of boron-doped graphite. *Carbon*. 37(2): 293-299.
- [46] Halford, Bethany. 2005. Unusual properties of nanotubes made from inorganic materials offer intriguing possibilities for applications. *Chemical and Engineering News*. 83(35): 30-33.
- [47] Hirsch, A., M. Brettreich, F. Wudl. 2005. *Fullerenes: Chemistry and Reactions*. Wiley-VCH, Germany.
- [48] Ltaief, A., A. Bouazizi, J. Davenas, P. Alcouffe, R. Ben Chaabane. 2006. Dielectric behaviour of polymer-fullerene composites for organic solar cells. *Thin Solid Films*. 511-512: 498-505.
- [49] Al Rasheed RA. Wastewater treatment by heterogeneous photocatalysis, an overview. In: Presented at the 4th SWCC acquired experience symposium. Jeddah; 2005.
- [50] Lvayen, V., E. Benavente, C.M. Sotomayor Torres, G. Gonzalez. *Inorganic Fullerenes: From lamellar Precursors to Functionalized Nanotubes*. *Solid State Phenomena*. 121-123: 1-4, 2007..
- [51] Nierengarten, J., M. Gutierrez-Nava, S. Zhang, P. Masson, L. Oswald, C. Bourgogne, Y. Rio, G. Accorsi, N. Armaroli, S. Setayesh. 2004. Fullerene-containing macromolecules for materials science applications. *Carbon*. 42(5-6).
- [52] Parilla P.A., A. C. Dillon, K. M. Jones, G. Riker, D. L. Schulz, D. S. Ginley, M. J. Heben. 1999. The first true inorganic fullerenes? *Nature*. 397(114).