Effects of alcohols on shape-tuning and luminescence-enhancing of C$_{70}$ nanocrystals

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Abstract:
C$_{70}$ nanotubes, nanorods and nanoparticles were produced by introducing a series of alcohols as precipitant into a C$_{70}$/m-xylene solution. The effects of alcohols with different carbon chain lengths on the shape control of C$_{70}$ nanocrystals were investigated. Alcohols with more than two carbon atoms in the longest chain linked to the hydroxyl groups induced the formation of C$_{70}$ nanotube/rods. In contrast, alcohols containing two or fewer carbon atoms resulted in C$_{70}$ nanoparticles. Structural analysis indicated that alcohol molecules exist in the C$_{70}$ nanocrystals, forming solvated structures. The freshly formed C$_{70}$ nanotubes and nanoparticles have orthorhombic and hexagonal solvated structures, respectively. Room temperature photoluminescence was further carried out on the solvated C$_{70}$ nanocrystals to investigate their optical properties. We found that the luminescence intensities of C$_{70}$ nanocrystals were significantly enhanced by the introduction of alcohols.

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Fullerenes, typical zero-dimensional materials, have attracted much attention since their discovery in 1985 [1]. In recent years, synthesis of low-dimensional nanocrystals with individual fullerene molecules as building blocks has aroused a research fever of nanotechnology [2–6]. Several methods, such as the use of templates [5] solvent-assisted methods with a solution or vapor–solid processes [2,3,6,7], have been used to synthesize fullerene crystals with various shapes and morphologies. Among these methods, the solvent-assisted method is reported to be a convenient and efficient method, which has become widely used for the synthesis of fullerene crystals. Early work reported the synthesis of large-size C$_{60}$ crystals (a few hundred micrometers in size) by using dichloromethane [7], 1,1,1-trichloroethane [8], benzene [9], etc., as solvents. Recent studies focused on the synthesis of fullerene crystals with sizes in the submicro/nanometer range, such as nanosheets, nanowhiskers, nanotubes and nanorods [2,3,5–7]. In general, in such a typical solvent-assisted synthesis process, one single solvent or two collaborative solvents were employed, playing a decisive role on the formation of fullerene nanocrystals. For example, we found that m-xylene is a good controller for fabricating well dispersed and highly crystalline C$_{60}$ nanorods and nanosheets directly on different substrates using an easy solution evaporation method [6]. C$_{60}$ nanowires with a V-shaped cross section were also prepared from a 1,2,4-trimethylbenzene solution of C$_{60}$ [10]. Such solvents, containing p-aromatic rings, are efficient aids in assembling fullerene molecules into micro/nanocrystals. This can be understood from their high chemical affinity to the fullerene, probably due to the strong interactions between their p aromatic rings (the outer surface of a C$_{60}$ molecule is covered with p electrons and appears to be aromatic). On the other hand, the synthesis of C$_{60}$ nanowhiskers or tubes by adding precipitant into C$_{60}$/m-xylene or C$_{60}$/toluene solutions has been also reported [7,11], providing a new effective way to fabricate C$_{60}$ nanocrystals. Alcohols, as “poor solvents” of fullerene, are usually used as such precipitants together with aromatic solvents in many experiments for fullerene nanocrystal synthesis. In recent reports, Sathish and Miyazawa found that the sizes of hexagonal crystalline C$_{60}$ nanosheets could be tailored at the carbon tetrachloride (CCl$_4$)/alcohol interface by changing the kind of alcohol, although the size tuning mechanism was not understood [12]. Very recently, Jeong et al. obtained irregular C$_{60}$ microcrystals, microplates and microrods by adding ethanol, 1-propanol, and 1-butanol, respectively, into a C$_{60}$ solution in toluene [13]. They believe that the different supersaturations of C$_{60}$ solutions mixed with different alcohols may be the reason for the different crystal morphologies. In
contrast, alcohols were also considered to behave as nucleation agents of $C_{60}$ crystals in the process of crystal formation [14]. However, only a few alcohols were analyzed for the fabrication of fullerene nanocrystals, and even for these alcohols the detailed shape tuning mechanism was not clear. Thus, more systematic investigations are urgently needed to clarify what types of alcohols could be used to tune fullerene crystals to certain morphologies and how they affect the crystal morphologies.

As we know, $C_{70}$ is the second most abundant fullerene, and many of its properties are superior to those of $C_{60}$, such as good fluorescence, conductivity, photoconductivity and optical limiting performance [15–18]. For practical applications, it is more important to fabricate $C_{70}$ crystals. However, less work has been done on the fabrication of $C_{70}$ nanocrystals, possibly because of its elliptical molecular structure and relatively strong polarity, making it more difficult to control the assembling of $C_{70}$ molecules. We have obtained $C_{70}$ nanorods [19] by slow evaporation of a $C_{70}$ solution in $m$-xylene. Miyazawa et al. also observed $C_{70}$ crystals with tubular structures among $C_{70}$ fibers through the cooperation of pyridine and isopropyl alcohol or isobutyl alcohol [20,21]. Nevertheless, tuning the $C_{70}$ crystals to a desired shape and size is still being explored and is one of the key factors in pushing $C_{70}$ into practical applications. Here, we have made efforts to tune the shape and size of $C_{70}$ micro/nanocrystals by adding various alcohols into a $C_{70}/m$-xylene solution, trying to understand how the alcohols affect the packing of $C_{70}$ molecules and the structure of $C_{70}$ nanocrystals. In addition, to understand the nature of the interactions between $C_{70}$ and the alcohol molecules, it is also very important to identify the positions occupied by the different alcohol molecules in the $C_{70}$ lattice. This could help us determine the relationship between the structures and morphologies of these nanocrystals.

On the other hand, due to its relative lower molecular symmetry comparing to $C_{60}$, the luminescence of $C_{70}$ is slightly stronger than $C_{60}$. However, it is still not enough to be used in practical application, to enhance the intensity of $C_{70}$ crystals is thus still a necessary task. Previous reports suggested that when fullerenes were polymerized, their molecular symmetry will decreased, which could improve their PL intensities [22–24]. Nevertheless, when fullerenes are polymerized their band gaps would also be changed, resulting in a change of their luminescence wavelengths [22–24]. In our recent work, we have found that introduction of $m$-xylene into $C_{60}$ nanorods is effectual for enhancing luminescence, which do not change
its initial luminescence wavelength [25]. And whether the introduction of organic solvents is effective to improve the luminescence properties of C\textsubscript{70} crystal is still an open question.

We have studied eight kinds of alcohols with different geometries as shape tuners to synthesize C\textsubscript{70} crystals. C\textsubscript{70} crystals with different sizes and shapes have been obtained, depending on the alcohols used. In particular, C\textsubscript{70} nanotubes were successfully obtained by selecting several alcohols with proper alcohol/solvent volume ratios. It was found that the number of carbon atoms in the longest chain linked to the hydroxyl (–OH) groups plays a key role in the formation of C\textsubscript{70} nanotubes, when this number is larger than two, C\textsubscript{70} nanotubes with uniform shapes and sizes were successfully obtained. On the other hand, when this number is equal or less than two, C\textsubscript{70} nanoparticles were obtained. Structural analysis shows that the C\textsubscript{70} crystals obtained using alcohols with more than two carbon atoms have an orthorhombic structure, whereas the crystals obtained using alcohols with less than two carbon atoms have a hexagonal structure. We propose a tentative mechanism for the tuning effect of alcohols on the shape of C\textsubscript{70} single nanocrystals, which would be very useful as guidance for future synthesis of C\textsubscript{70} nanocrystals. Furthermore, we have also recorded the PL spectra of C\textsubscript{70} nanocrystals. The luminescence intensities of C\textsubscript{70} nanocrystals have been highly enhanced by the introduction of alcohols.

2. Experiment section

2.1. Preparation of C\textsubscript{70} nanocrystals with different morphologies

C\textsubscript{70} nanotubes were fabricated by modifying our solution evaporation method for C\textsubscript{70} nanorod synthesis by introducing various kinds of alcohols into saturated C\textsubscript{70}/m-xylene solution. Eight kinds of alcohols were studied in our experiment, including methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butanol, isobutyl alcohol, 2-butyl alcohol and tertbutyl alcohol. During the experiment, the mixed solution of C\textsubscript{70}/m-xylene and alcohols was left to evaporate at room temperature for 5 h, after which C\textsubscript{70} nanocrystals with various shapes were obtained at the bottom of the bottles. The as-grown samples were heated at 150 °C in vacuum (10^{-4} Pa). To study the shape tuning effect of different alcohols, we carried out two sets of experiments, one by changing the series of alcohols in the mixed solution, using a fixed volume ratio of
1:10; and the other one by adjusting the volume ratio from 1:5 to 1:50 for some of these alcohols to optimize the conditions for synthesis of high quality C\textsubscript{70} nanotubes.

2.2. Characterization and PL properties of C\textsubscript{70} nanocrystals

The samples obtained were characterized by transmission electron microscopy (TEM, JEM-2010, Japan), infrared spectroscopy (IR, Nicolet Avatar 370 DTGS), and X-ray diffraction (XRD, Rigaku D/max-RA). The Raman and PL spectra of the nanotubes and pristine C\textsubscript{70} were obtained using a Raman spectrometer (Renishaw inVia, UK) with 830 nm and 514.5 nm lasers as excitation, respectively.

3. Results and discussions

Fig. 1a–d shows typical TEM images of nanocrystals obtained using several kinds of alcohols, with the volume ratio of \textit{m}-xylene/alcohol fixed to 1:10. Three kinds of morphologies of the samples were observed for the samples: nanoparticles, nanorods and nanotubes. Fig. 1a shows the TEM image of samples produced with methanol as the shape tuner. The image reveals that the C\textsubscript{70} crystals have a nanoparticle morphology with diameters in the range of 200–400 nm. The general morphologies of the samples obtained using isobutyl alcohol and isopropyl alcohol are shown in Fig. 1c and d, the insert of Fig. 1c showed the magnified images of sample tips, which exhibited a tubular shape. Here, nanotubes and rods with diameters in the ranges of 300–800 nm and 500–700 nm were observed, respectively. The size and length of the nanotubes obtained from isopropyl alcohol were much more regular than those obtained using other alcohols. Fig. 1b shows a TEM image of products obtained using ethanol, for which a mixture of C\textsubscript{70} nanoparticles and short rods were observed. High magnification TEM images and selected area electron diffraction patterns (SAEDs) of single as-grown and heat-treated C\textsubscript{70} nanotubes are shown in Fig. 1e and f, respectively. The SAED patterns indicate that both of them are highly crystalline single crystals. According to the XRD results shown below, it is found that the longitudinal axes of the as-grown and heat-treated C\textsubscript{70} nanotubes are paralleled to the (110) orientation of the tubes’ orthorhombic and fcc structure, respectively.
By carefully observing C\textsubscript{70} nanocrystals obtained using various alcohols we can summarize the morphologies of the samples and the alcohols employed in Fig. 2, where we have classified the alcohols into three groups based on the length of the main chain linked to the hydroxyl group. As shown in this figure, an increase in the main chain length of the alcohols from 1 to 4 carbon atoms leads to an obvious shape evolution of the products, from nanoparticles (Fig. 1a) to nanoparticles and short rods (Fig. 1e), and finally to nanorods and nanotubes (Fig. 1c and d). It is clear that when the number of carbon atoms in the main chain of the alcohol is larger than two, it leads to the formation of C\textsubscript{70} nanotubes. For the alcohols having two carbon atoms or less in the main chain, only C\textsubscript{70} nanoparticles could be obtained. Furthermore, between methanol and isopropyl alcohol, there are only two carbon atoms but no branched chain in the ethanol molecule. It is found that the crystal morphology obtained using ethanol begins to change from particle to a quasi-one-dimensional (1D) structure. The above results indicate that the morphologies of C\textsubscript{70} nanocrystals depend on the main chain length of the alcohol molecules, and that C\textsubscript{70} nanotube/rods can only be obtained when the alcohols have more than two carbon atoms.

Among the C\textsubscript{70} nanotubes fabricated with a fixed volume ratio of 1:10, a uniform size and shape was observed for the sample obtained using isopropyl alcohol. The sizes of the nanotubes obtained from other alcohols in Group 3 in this condition varied over a relative large range, and nanorods were also found in the samples. Whether pure C\textsubscript{70} nanotubes with uniform shapes could be fabricated from all these alcohols is still an open question. To obtain pure C\textsubscript{70} nanotubes with regular size and length using other alcohols, we carried out more detailed studies by varying the volume ratio of \textit{m}-xylene/alcohols. Fig. 3a–d shows TEM images of samples obtained by mixing C\textsubscript{70}/\textit{m}-xylene saturated solution with 2-butyl alcohol in volume ratios of 1:5, 1:15, 1:20 and 1:50. As shown in Fig. 3a, nanotubes with diameters in a large range of 400–1500 nm, and lengths in the range of 5–30 μm were obtained using a volume ratio of 1:5. When the volume ratio was 1:15, we obtained nanotubes with diameters in the range of 500–700 nm and lengths in the range of 3–5 μm, which we would consider as uniform lengths and diameters. However, when the volume ratio was decreased to 1:20 and 1:50 (Fig. 3c and d), solid nanorods were fabricated instead of hollow nanotubes. Similar experiments were also carried out using n-propyl alcohol and tertbutyl alcohol, and uniform nanotubes were again obtained when using these alcohols in proper volume ratios. From these results, we conclude that the volume ratio of \textit{m}-xylene/alcohols significantly affects both the
shapes of the C_{70} nanocrystals and the size distribution of C_{70} nanotubes, and that there is an optimum ratio which produces high quality C_{70} nanotubes for each alcohol in Group 3.

3.1. Raman spectroscopy

Raman spectroscopy is a powerful tool to characterize C_{70}. Due to the reduced symmetry of the C_{70} molecule compared to the C_{60} molecule, the number of vibrational modes of this molecule increases dramatically. For pure C_{70} at room temperature, 53 Raman active modes are predicted (12A’_1 + 22E’_2 + 19E’_1) from the D_{5h} point group according to group theory [26]. As shown in Fig. 4, the Raman spectra of as-grown C_{70} nanocrystals fabricated from different alcohols were recorded. More than twenty peaks were found in the Raman spectrum of the nanocrystals. A direct comparison of the spectra to bulk crystals shown in curve A, we found an excellent agreement with that of pristine C_{70} bulk materials, indicating that the nanotubes really consist of C_{70}. Furthermore, for all samples, the peak assigned to be one of the E’_2 modes was found at 1567 cm\(^{-1}\), the same Raman shift value as in the experimental results of Chandrabhas et al. [27] and the calculated results of Jishi et al. [28]. This peak is characteristic for pristine C_{70} and it is well known from literature that it splits into two peaks in polymerized C_{70} [29,30]. The presence of this single peak further indicates that the C_{70} nanotubes consist of monomeric C_{70}.

3.2. Infrared spectroscopy

To further explore the shape tuning mechanism of alcohols, it is necessary to investigate the components of the as-grown samples. IR spectroscopy is considered as an effective tool to characterize organic solvents, and was thus used to study the components of the C_{70} solvates. Fig. 5 shows typical IR spectra for as-grown nanotubes obtained using (A) isopropyl alcohol and (B) isobutyl alcohol, and nanoparticles obtained using (C) ethanol and (D) methanol. About 10 peaks indexed to the absorption peaks of C_{70} were observed in the range 500–1500 cm\(^{-1}\) for all the four samples, which further verifies that all these samples consist of C_{70}. Furthermore, three wide absorption bands marked with ‘‘N’’ were found in the ranges 900–1200 cm\(^{-1}\), 2800–3000 cm\(^{-1}\) and 3000–3700 cm\(^{-1}\), respectively, and were assigned to be the absorption bands of alcohols [31]. The IR spectra indicate that part of the alcohols remained trapped in the C_{70} nanocrystals during the formation process. In addition, curve E shows the IR spectrum for samples obtained using isopropyl alcohol, and heat treated at 150° C, in
vacuum. It is obvious that all the IR peaks attributed to the solvents could not be observed in the spectrum, indicating that the solvents could be driven out the sample under this condition.

To investigate the relationship between the shapes of the C\textsubscript{70} nanocrystals and the content of alcohols, we compared the relative intensities of the three peaks assigned to alcohols. For example, we investigated the ratio between the intensity of the strongest peaks for the alcohols in the range 3000–3700 cm\textsuperscript{-1} and that of C\textsubscript{70} at 1430 cm\textsuperscript{-1} in different crystals. This ratio is 0.34 (A), 0.7 (B), 4 (C) and 4.3 (D), respectively. It is obvious that the relative intensities of all the three absorption peaks for alcohols in the spectra of C\textsubscript{70} nanoparticles are much stronger than those observed for nanotubes, indicating that the relative contents of alcohols were much larger in C\textsubscript{70} nanoparticles than in nanotubes. From the IR results we found that the shapes of the C\textsubscript{70} crystals have a strong correlation with the content of the different alcohols trapped in the crystals.

3.3. X-ray diffraction

To investigate how the solvent molecules were introduced in the C\textsubscript{70} nanocrystal lattice, we investigated the crystal structures of the as-grown C\textsubscript{70} crystals with different morphologies by XRD. Here we present representative XRD patterns for the as grown C\textsubscript{70} nanotubes obtained using isopropyl and isobutyl alcohol in Fig. 6, curves C and D. The structure of the solvated C\textsubscript{70} nanotubes has been indexed as an orthorhombic system with cell dimensions a\textsubscript{O} = 1.534 nm, b\textsubscript{O} = 1.594 nm, c\textsubscript{O} = 1.793 nm for the isopropyl derived material, and a\textsubscript{O} = 1.577 nm, b\textsubscript{O} = 1.528 nm, c\textsubscript{O} = 2.228 nm for the isobutyl solvate. According to the diffraction shown as curve B in Fig. 6, the structure of C\textsubscript{70} nanoparticles obtained from methanol is indexed as a hexagonal structure with cell dimension a\textsubscript{H} = 1.154 nm and c\textsubscript{H} = 1.744 nm. For comparison, the XRD pattern for bulk C\textsubscript{70} single crystal is also shown (curve A) and is found to have a hexagonal structure with a\textsubscript{H} = 1.114 nm and c\textsubscript{H} = 1.758 nm, which is slightly different from the parameters of C\textsubscript{70} bulk crystal reported before. [32] The XRD results indicated that all the as-grown nanotubes obtained from different alcohols have orthorhombic structures, while as-grown C\textsubscript{70} nanoparticles have a hexagonal structure similar to that of bulk crystals. In addition, we also studied the structure of pure C\textsubscript{70} nanotubes without solvent, after being treated at 150\textdegree{}C in vacuum. In the XRD pattern shown in Fig. 5 curve E, there are three diffraction peaks which were indexed as the (111), (220), (311) diffraction peaks of an fcc lattice. The cell parameter of the fcc structure is a\textsubscript{F} = 1.49 nm. This result indicates that pure
C\textsubscript{70} nanotubes with fcc structure were successfully obtained through such gentle treatment conditions, consistent with our TEM observations. Also, Fig. 5 curve E shows the XRD pattern of C\textsubscript{70} nanoparticles obtained using methanol following by heat treatment at 150\degree C in vacuum. This pattern is almost the same with that of the heat-treated C\textsubscript{70} nanotubes. These results further suggest that all the C\textsubscript{70} nanocrystals have a similar fcc structure after this general treatment.

3.4. PL properties of alcohol introduced C\textsubscript{70} nanocrystals

To investigate the luminescence properties of samples, we have carried out the PL spectra of the as-grown C\textsubscript{70} nanocrystals under ambient conditions, with identical excitation laser power. PL spectra of C\textsubscript{70} nanocrystals fabricated from methanol, (D) ethanol, (B) isopropanol (C) and isobutyl alcohol (E) are shown in Fig. 7. For comparison, PL spectrum of pristine C\textsubscript{70} bulk crystals was also exhibited as curve (A). The main PL peak of C\textsubscript{70} bulk crystals is at the position about 720 nm, and the positions of strongest peaks in all the spectra of C\textsubscript{70} nanocrystals are similar to that of bulk crystals. This suggests that the strong luminescence originates from C\textsubscript{70} itself, and the doping of alcohols do not change the band gap of C\textsubscript{70} nanocrystals. As is known to us, due to their symmetry restrictions, the luminescence intensity of pristine pure fullerene crystals is very low at room temperature [33,34]. However, by careful observation of the PL spectra of all our samples, we found that the highest intensities were 160,980 a.u., 156,893 a.u., 98,199 a.u., 96,820 a.u. and 19,071 a.u., for curve E, D, C, B and A, respectively. The relative PL intensities ratio is about 8.5:8.3:5.2:5.1:1. It is obvious that the intensities of the C\textsubscript{70} nanocrystals are one order of magnitude higher than for pristine bulk crystals. From the above discussion, we have known that alcohols have been introduced into the lattice of C\textsubscript{70} nanocrystals. Here, the enhancement of luminescence intensities is probably induced by the decreasing of molecular symmetry results from the introduction of alcohols. This result is in good agreement with that of m-xylene doped C\textsubscript{60} nanorods [25]. To prove this conclusion, the PL spectrum of C\textsubscript{70} nanotubes treated at 150\degree C in vacuum, which was pure without any solvent, was added in Fig. 7F. The PL intensity of the pure C\textsubscript{70} nanotubes was 25,103 a.u., close to that of bulk crystals, and much lower than that of solvated samples. This result indicated that the introduction of solvent play the key role for the enhancement of luminescence. In particular, for C\textsubscript{70} nanocrystals obtained from methanol and isobutyl alcohol, the intensities are even stronger than those for ethanol and isopropanol. It is also known that the polarity of methanol is strongest among all the alcohols and the size of
isobutyl alcohol is largest in these four alcohols, the introduction of these two alcohols could probably influence the molecular symmetries of C\textsubscript{70} more greatly, the stronger PL intensities observed for these two samples is thus reasonable.

4. Conclusion

We have synthesized C\textsubscript{70} nanocrystals by modifying the solution method. The shapes of the C\textsubscript{70} crystals produced has been tuned appropriately by introducing different alcohols into the C\textsubscript{70}/m-xylene solution, and the size of the C\textsubscript{70} nanotubes obtained was tuned by changing the volume ratio of alcohols and m-xylene. We found that carbon chain length in alcohol molecules plays a vital role in the formation of the 1D structure. Alcohol molecules having more than two carbon atoms were introduced into the C\textsubscript{70} lattice to form an orthorhombic structure, causing the formation of the 1D structure, whereas alcohol molecules having two or less carbon atoms introduced into the interstitial voids of lattice, causing the formation of particle shapes. We have also recorded the PL spectra of as-grown C\textsubscript{70} nanocrystals obtained from different alcohols. The PL intensities of solvated C\textsubscript{70} nanocrystals were highly enhanced by the introduction of alcohols. This is due to the decrease C\textsubscript{70} molecular symmetry, which has great relationship with the molecular size and polarities of introduced alcohols. This work provides a new approach to tune the shapes of C\textsubscript{70} nanocrystals and suggests a correlation between the sizes of alcohol molecules, the structures and the morphologies of C\textsubscript{70} nanocrystals. It should be useful for the fabrication of building blocks with potential application in nano-devices.

Acknowledgments

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References:

FIGURE CAPTIONS:

Fig. 1. TEM images of C\textsubscript{70} nanocrystals fabricated by mixing a saturated C\textsubscript{70}/m-xylene solution with (a) methanol, (b) ethanol, (c) isobutyl alcohol, and (d) isopropyl alcohol in a fixed volume ratio of 1:10. We also show TEM image and SAED for single (e) as-grown and (f) heat-treated C\textsubscript{70} nanotube obtained using isopropyl alcohol.

Fig. 2. Morphologies of the synthesized samples and the molecular structures of the alcohols employed. The length of the alcohol molecules is the distance between the oxygen atom and the farthest carbon atom in the main chain.

Fig. 3. TEM images of C\textsubscript{70} nanocrystals fabricated by mixing C\textsubscript{70}/m-xylene saturated solution with 2-butyl alcohol in the volume ratios (a) 1:5, (b) 1:15, (c) 1:20 and (d) 1:50.

Fig. 4. Raman spectra of C\textsubscript{70} bulk crystals (A), as-grown nanocrystals fabricated from methanol (B), ethanol (C), isopropanol (D) and isobutanol (E).

Fig. 5. IR spectra of as-grown nanotubes obtained using (A) isopropyl alcohol and (B) isobutyl alcohol, and nanoparticles obtained from (C) ethanol and (D) methanol. Curve (E) shows the IR spectrum of C\textsubscript{70} nanotubes obtained using isopropyl alcohol, and heat treated at 150° C, in vacuum.

Fig. 6. XRD patterns for (A) pristine C\textsubscript{70} bulk crystal, (B) as-grown nanoparticles obtained using methanol, and C\textsubscript{70} nanotubes obtained using (C) isopropyl alcohol and (D) isobutyl alcohol. (E) C\textsubscript{70} nanotubes heat-treated at 150° C in vacuum.

Fig. 7. PL spectra of C\textsubscript{70} bulk crystals (A), nanocrystals obtained from ethanol (B), isopropanol (C), isobutyl alcohol (D) and methanol (E).
FIGURE 1.
<table>
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<tr>
<th>Group 1</th>
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<th>Length of molecules</th>
<th>Morphology of Samples</th>
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**FIGURE 2**

![Images of different samples](a)(b)(c)(d)

**FIGURE 3**