

Short note

About the formation of C₆₀ fine particles with reprecipitation method in ethanol/carbon disulfide mixture

L. Zulian^{a,b,*}, B. Ruzicka^{b,c}, G. Ruocco^{b,c}

^a Dipartimento di Fisica, Università di Perugia, via A. Pascoli, I-06123 Perugia, Italy

^b CRS SOFT CNR-INFN, Italy

^c Dipartimento di Fisica, Università di Roma "La Sapienza", P.zze A. Moro 2, I-00185 Roma, Italy

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Abstract

We present a short communication to discuss some of the results of two works by Fujitsuka et al. [M. Fujitsuka, H. Kasai, A. Masuhara, S. Okada, H. Oikawa, H. Nakanishi, A. Watanabe, O. Ito, Chem. Lett. (1997) 1211; M. Fujitsuka, H. Kasai, A. Masuhara, S. Okada, H. Oikawa, H. Nakanishi, O. Ito, K. Yase, J. Photochem. Photobiol. A 133 (2000) 45] in which the photochemical and photophysical properties of a dispersion of fullerene fine particles are discussed. One of the simplest way to growth organic fine particles is the reprecipitation method. In this way microcrystals of fullerene molecules can be obtained with a good control on dimension and size distribution of the final aggregates. The existence and the distribution of fullerene clusters in these liquid solutions is usually attained and characterized by dynamic light scattering technique. In this short communication we want to address a common mistake derived from the widely used reprecipitation method. We show that photoncorrelation measurements from [M. Fujitsuka, H. Kasai, A. Masuhara, S. Okada, H. Oikawa, H. Nakanishi, A. Watanabe, O. Ito, Chem. Lett. (1997) 1211; M. Fujitsuka, H. Kasai, A. Masuhara, S. Okada, H. Oikawa, H. Nakanishi, O. Ito, K. Yase, J. Photochem. Photobiol. A 133 (2000) 45] are faulty due to the presence of a microemulsion between the two solvents used. In ethanol/carbon disulfide mixtures, CS₂ droplets dispersed in ethanol mimic in fact the existence of ≈ 300 nm clusters which, actually, do not exist.

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Fullerenes and carbon nanotubes are currently of great interest in many technological and scientific areas due to their unique chemical and physical properties. Among different important phenomena related to the physics and chemistry of fullerenes, the possible spontaneous formation of large molecular aggregate (clusters) when fullerene C₆₀ is dissolved in a liquid is of great interest. The first evidence of formation of fullerene aggregates in solution was provided by studies on the temperature dependence of the solubility of C₆₀ [3]. The aggregation phenomenon of C₆₀ has been later observed and studied in a variety of solvents and mixture of solvents with different techniques as, for example, optical absorption, TEM microscopy, static and dynamic light scattering [5–13]. The size of the aggregates has

been found variable between about 10 nm and 1 μm, depending on the nature of the solvent and on the fullerene concentration.

Inorganic nanocrystals have attracted a lot of interest because of their size dependent properties and for the understanding of their physical and chemical phenomena. Studies about the quantum confinement effect [14] and its application in non linear optics [15] have been performed on these materials. Moreover organic fine particles can be regarded as new interesting materials with a wide open field of investigation. Fullerene C₆₀ aggregates can be considered one of the candidates for this organic fine particles. One of the methods described in the literature for the preparation of organic fine particles is the reprecipitation method [16]. In a typical reprecipitation experiment the solution of the organic material in a good solvent is dispersed dropwise into a different right solvent. The final solution is vigorously stirred for few minutes and then the dispersion of microcrystals with dimensions depending on the concentration of the organic material in the first solution is obtained. In the specific case

* Corresponding author at: Università "La Sapienza", Dipartimento di Fisica, Ed. Fermi, Piazzale Aldo Moro 5, I-00185, Roma, Italy. Tel.: +39 06 49913505; fax: +39 06 4463158.

E-mail address: laura.zulian@roma1.infn.it (L. Zulian).

of C₆₀ we referred to the sample preparation described in two papers by Fujitsuka et al. [1,2]. In this work we want to discuss about some results obtained in these two papers and about the goodness of the reprecipitation method to obtain C₆₀ fine particles with the combination of solvents used. In particular in the following, we will show, with simple argumentations, that fine particles with a radius revealable with light scattering technique are not obtained. Furthermore the results reported in literature [1,2] can be explained with the formation of a microemulsion between the two solvents used. The materials used, all from Sigma–Aldrich, are CS₂ (HPLC grade, 99.9 + %) and pure ethanol, as solvents, and buckminsterfullerene C₆₀ powder 99.5% as solute. We first prepare a solution 0.1 mM of C₆₀ in CS₂ where carbon disulfide is one of the best solvent for the fullerenes (solubility [C₆₀]_{CS₂} = 7.9 mg/mL [3,4]). The solution is easily obtained mixing the weighted quantity of C₆₀ powder in the solvent and stirring for few minutes. Following the procedure described in [1,2], the microcrystal dispersion of fullerenes is obtained injecting 0.2 mL of this C₆₀CS₂ solution into 10 mL of pure ethanol (bad solvent for C₆₀ powder: solubility [C₆₀]_{EtOH} = 0.001 mg/mL [3,4]) under continuous stirring at room temperature (C₁ sample). After this treatment the mixture appears transparent and practically colorless while the solution of C₆₀ in carbon disulfide has a strong violet color. A second kind of sample is also prepared following the same method of preparation, mixing 0.2 mL of pure CS₂ solvent in 10 mL of ethanol through vigorous stirring at room temperature (C₂ sample). The final solution, also in this case, is totally transparent and colorless.

Dynamic light scattering measurements were performed using an ALV-5000 logarithmic correlator in combination with a standard optical setup based on an He–Ne ($\lambda = 632.8$ nm) 10 mW laser and a photomultiplier detector. The intensity correlation function was directly obtained as:

$$g_2(q, t) = \frac{\langle I(q, t)I(q, 0) \rangle}{\langle I(q, 0) \rangle^2}, \quad (1)$$

where q is the modulus of the scattering wave vector defined as $q = (4\pi n/\lambda) \sin(\theta/2)$ with $\theta = 90^\circ$ in this experiment. The dynamic structure factor $f(q, t)$ can be directly obtained inverting the Siegert relation:

$$f(q, t) = \sqrt{\frac{g_2(q, t) - 1}{b}}, \quad (2)$$

where b represents the coherence factor.

Ultraviolet–visible(UV–vis) absorption spectra were measured through a standard apparatus HP 8452A Diode Array Spectrophotometer with an accessible range between 190 and 820 nm and a resolution of 2 nm. The measurements were performed using quartz cuvettes of 1 mm thickness.

Fujitsuka et al. [1,2] performed dynamic light scattering and TEM microscopy measurements on a sample, identical to our C₁ sample, to probe the existence and the dimension of fullerene fine particles in the dispersions. Using a typical light scattering apparatus, the authors found a population of C₆₀ clusters with a narrow distributed dimensions centered at roughly 270 nm. These results seem to be confirmed by TEM measurements on

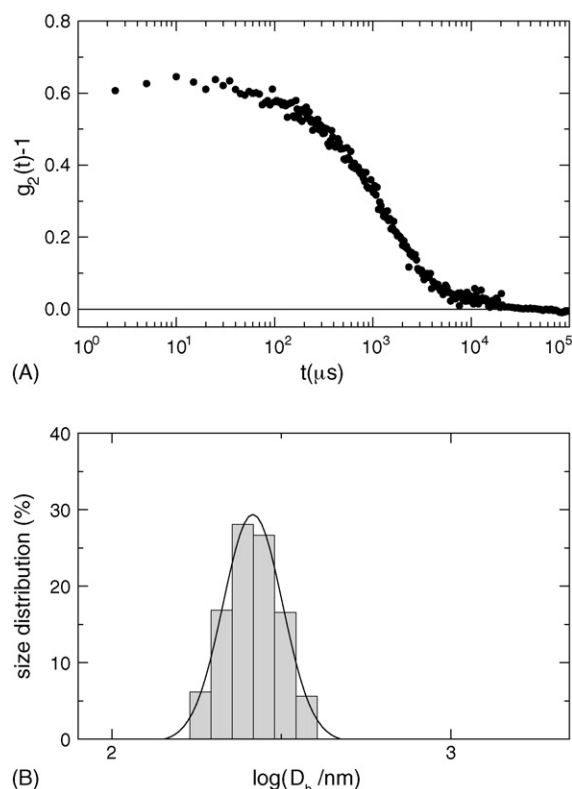


Fig. 1. (A) Homodyne autocorrelation function of the C₁ sample, obtained with vigorous stirring of 0.2 mL of C₆₀CS₂ solution 0.1 mM and 10 mL of pure EtOH. (B) Size distribution of particles in C₁ sample.

the same sample, that show granular objects with dimension of ~ 200 nm.

In Fig. 1A the measured homodyne normalized autocorrelation function relative to dispersions of C₆₀CS₂ solution in ethanol is shown (C₁ sample). We can obtain the hydrodynamic mean diameter of the hypothesized fullerene clusters distribution using the nonnegatively constrained least-squares (NNLS) program software analysis of the experimental curve (provided with the Brookhaven Instruments software package). The size distribution of the objects in the sample is reported in Fig. 1B. The mean hydrodynamic diameter is 270 nm and it is consistent with the results obtained by Fujitsuka et al. [1,2].

The same measurements of the dynamic structure factor are performed on the sample C₂. A comparison of the autocorrelation functions relative to C₁ and C₂ samples is shown in Fig. 2.

It is evident from Fig. 2 that the spectrum from the sample with supposed fullerene clusters of ~ 270 nm diameter and the one obtained from the sample without addition of C₆₀ molecules are superimposed as can be also confirmed from the data analysis.

For both samples the signal changes with time. The time evolution of the signal's intensity is the same for the two samples, it decreases until totally disappearing after roughly one day from sample preparation. If the samples are stirred again before the whole disappearance of the DLS signal, the intensity is recovered to the initial value and follows the same time evolution. On the contrary, if the agitation is performed after the disappearance of

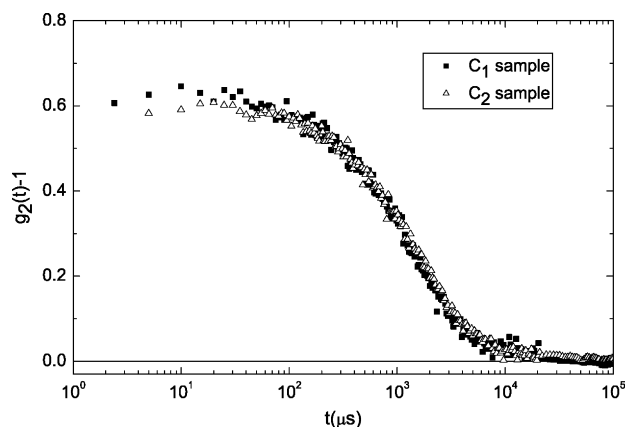


Fig. 2. Normalized homodyne autocorrelation functions of the two samples studied C_1 (■) with fullerenes, and C_2 (△) same sample without fullerenes.

the DLS signal, we cannot regain the initial condition and we do not observe any autocorrelation curve.

In Fig. 3 the UV–vis absorption spectra of the C_1 (solid line) and the C_2 (dotted line) samples are shown. The absorption spectra of the two samples are almost identical except for a well defined peak evident in the spectrum of the C_1 sample at 410 nm. The same peak is present in the spectrum of the molecular C_{60} in carbon disulfide ($C[C_{60}] = 0.1$ mM) reported in the inset of Fig. 3. A similar spectrum of molecular fullerene in benzene is also displayed by Fujitstuka in Fig. 1 of [1] and in Fig. 2 of [2]. We can speculate that the peak at 410 nm is due to the presence of molecules of C_{60} in sample C_1 . In the visible range the curves of C_1 (solid line) and C_2 (dotted line) samples are practically superimposed.

We propose that in reality the signal measured is due to the formation of a microemulsion between the two solvents used for the preparation of the samples: carbon disulfide and ethanol. Because of their chemical nature the two solvents are in fact not completely miscible, and the stirring during the preparation of the samples causes the formation of many little droplets of CS_2 in ethanol. Our measurements clearly show that this microemulsion evolves with time and that it is simply obtained

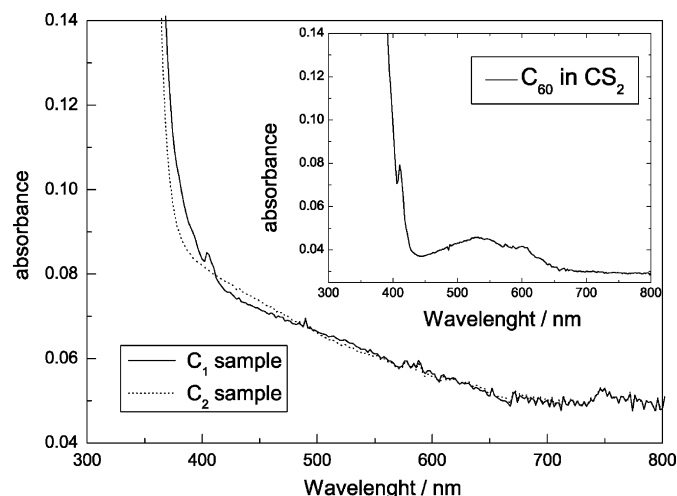


Fig. 3. Absorption spectra of C_1 sample (solid line) and C_2 sample (dotted line). Inset: absorption spectrum of C_{60} in CS_2 at 0.1 mM concentration.

with magnetic stirring or sonication. The decreasing of the scattering intensity observed during time is most likely due to the slow phenomenon of phase separation between the two solvents. If this phase separation was complete, also the stirring of the solution is unable to recover the initial microemulsion and no dynamic light scattering curve can be observed. On the contrary if the phase separation is not complete, with the sonication of the sample the intensity comes back to the initial conditions, because a microemulsion is again obtained, and it follows the same time evolution.

The presence of fullerene molecules does not change in any way the shape of the correlation function, as it is clear from Fig. 2. With our dynamic light scattering setup in the experimental conditions used ($T = 298$ K, $\eta_{\text{mix}} = C_{\text{EtOH}}\eta_{\text{EtOH}} + C_{\text{CS}_2}\eta_{\text{CS}_2} = 1.059$ mPa s, where C is the concentration of the species in the mixture and η is the viscosity) the accessible particles radius is between ~ 1 nm and $10 \mu\text{m}$. Then we are confident that if C_{60} clusters are present they must have a dimension smaller than the minimum revealable radius. Moreover, as proof of the existence of these aggregations in solution, TEM microscopy is used by Fujitstuka et al. [1,2] and several other experimental works, e.g. [5–7]. Nevertheless this technique needs to dry the sample with a possible morphological modification of the original liquid dispersion. The very fast evaporation of the solvent, should in fact induce the formation of C_{60} microcrystals as can be also observed putting a single droplet of $C_{60}CS_2$ solution on a microscope glass slide. Carbon disulfide has in fact a very low boiling point ($BP = 46^\circ\text{C}$) so the evaporation of the whole droplet is almost instantaneous. In this way one would mimic the effect of the dry treatment needed for TEM measurements. During the evaporation of the solvent, the formation of a yellow brownish C_{60} crystal with dimensions so big as some hundreds of nanometers can be observed with the aid of a microscope. For these reasons we think that in this case TEM microscopy is probably not the right experimental technique for probing the existence of microcrystals aggregates, because such measurements could be faulty.

Several research groups investigate today the presence and the properties of fullerene clusters in binary mixtures (for example [17–19]). In some cases C_{60} powder is solved in a good solvent and then the solution is mixed in a poor solvent for fullerenes. The aim of this comment is to recommend the researcher using this method to take care at the effective miscibility of the solvents used, in order to avoid the formation of microemulsions. As shown in this paper, the signal due to these microemulsions can be erroneously attributed to formation of fullerene clusters.

In conclusion, in order to confirm the real presence of fullerene clusters we have measured the dynamic structure factor of two kind of samples, prepared with the method of reprecipitation in pure ethanol of CS_2 with (C_1) and without (C_2) fullerene molecules inside. The comparison between the two experimental curves shows that the signal from the two samples are identical. We conclude that the observed behavior is totally due to the microemulsion formed between the two solvents. Moreover TEM measurements are not a conclusive experimental technique to reveal the presence of fullerene aggregates

in this specific case, because the dry of the sample needed is likely the cause of the formation of the microcrystals observed. Finally in the C₁ sample studied there are not fullerene clusters or if they are presents their dimensions are not wide enough to be observed with dynamic light scattering measurements. Finally we want to clarify that the erroneous determination of the particle size from [1,2] probably does not affect the validity of photochemical results presented in this two works.

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