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La@C_{82} as a spin-active filling of SWCNTs: ESR study of magnetic and photophysical properties

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Electron microscopy (TEM) and electron spin resonance (ESR) were applied to characterize lanthanum metallofullerene (La@C_{82})-filled peapods. The peapods were prepared by encapsulation of La@C_{82} in SWCNTs, which were obtained by laser ablation technique in the presence of non-magnetic catalysts Pt : Rh : Re. Empty fullerenes, C_{60}, were used as separators for the spin-active La@C_{82}. TEM analysis confirmed filling of peapods with both C_{60} and La@C_{82} molecules. ESR spectra acquired in the temperature range from 5 K to 295 K provided indirect evidence of encapsulation of the spin-active La@C_{82} in carbon nanotubes and pointed to marked differences in magnetic properties of peapods as a function of the relative concentration of La@C_{82}. Preliminary ESR studies of the photo-physical properties of La@C_{82} in CS_2 revealed that, under illumination with white light, La@C_{82} neither generated singlet oxygen nor was photoactive against a paramagnetic target, nitroxide radical (TEMPO).

1 Introduction There are many experimental works and theoretical proposals concerning exceptional electronic properties of carbon nanotubes (CNTs) and fullerenes. Recently, peapods, *i.e.* single walled carbon nanotubes (SWCNTs) filled with fullerene cages are getting increasing attention [1]. Since a chain of interacting spin-active molecules can be realized by filling a SWCNT, peapods filled with paramagnetic endohedral fullerenes are especially attractive. In particular, they offer a possibility of designing a variety of spin-active constructs with reasonably long electron spin-coherence times and the potential for remote and strength-controllable manipulations of spin-spin interactions. Therefore, some of these one-dimensional hybrid structures are considered as potential materials for quantum information processing [2]. The efficient encapsulation of spin-active endohedral fullerenes, *e.g.* N@C_{60}, Gd@C_{82}, Y@C_{82}, Sc@C_{82}, or Dy@C_{82}, in CNTs is believed to be the prerequisite for the design of building blocks of quantum computers [3].

Since its first purification and isolation in macroscopic amounts in 1991 by Smalley and coworkers [4], the endohedral La@C_{82} has become one of the most widely experimentally and theoretically studied metallo-fullerenes. The formal electronic structure of the endohedral La@C_{82} can be described as La^{3+}@C_{82}^{3-} [5]. In this configuration, the La atom transfers three of its valence electrons to the C_{82} cage, thus acquiring its preferred closed-shell state (+3, $\boldsymbol{S} = 0$), while the cage itself acquires the net spin of $\boldsymbol{S} = ½$. The resolved electron spin resonance (ESR) spectra recorded for degassed solutions of La@C_{82} in various organic solvents revealed eight major resonant features, thus pointing to the isotropic hyperfine coupling of the unpaired electronic spin to a nuclear momentum $\boldsymbol{I} = 7/2$ of the ^{139}La atom [6-8]. Therefore, the lanthanum-containing fullerene,

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La@C_{82}, can be considered as a ground-state doublet with its paramagnetism originating in an unpaired electron spin in the π-electron system of the carbon framework. This is in contrast to another extensively studied endohedral fullerene and candidate for designing qubits, N@C_{60}, which has only 2% of the unpaired electron spin density on the carbon cage [9]. However, similarly to N@C_{60}, the lanthanum-containing fullerene, La@C_{82}, reveals reasonably long relaxation times and has the potential for performing controllable interactions with other spins, thus providing an embodiment for quantum information processing. In comparison with N@C_{60}, La@C_{82} is also more readily available and chemically stable. Moreover, upon reduction or oxidation, La@C_{82} changes to even more stable diamagnetic anionic ($[La@C_{82}]^{-1}$) or cationic ($[La@C_{82}]^{+1}$) forms [10].

Here, we focus on preparation and preliminary characterization of peapods filled with the paramagnetic lanthanum metallo-fullerene, La@C_{82}. The successful filling of peapods with the spin-active La@C_{82}, as well as with the separating cages of empty C_{60} fullerenes, has been demonstrated by transmission electron microscopy (TEM). ESR provided evidence of paramagnetic filling in peapods and pointed to marked differences in magnetic properties of peapods containing various concentrations of the spin-active endohedral fullerenes, La@C_{82}.

Since elucidation of the physical properties and chemical reactivity of La@C_{82} is a challenge for developing new spin-active hybrid structures for quantum computing, we also preformed preliminary studies of the photosensitizing properties of La@C_{82} in the organic solvent, CS_2. To this end, we performed ESR reactive scavenging of electronically excited dioxygen (singlet oxygen, $^1\Delta_g$). In contrast to the ground state molecular oxygen (O_2, $^3\Delta_g^-$) which is a paramagnetic triplet, the excited singlet oxygen $^1\Delta_g$ is diamagnetic and is known for its strongly oxidative properties [11]. The enormous reactivity of $^1\Delta_g$ finds applications in bleaching and disinfection reactions, in many chemical syntheses, as well as in novel therapeutic modalities, like photodynamic therapy (PDT) [12]. Singlet oxygen is often formed from O_2 in light-activated processes in the presence of light-harvesting substances, the photosensitizers. Especially, fullerenes C_{60} and C_{70} possess useful photophysical properties to efficiently generate singlet oxygen. In such photo-stimulated reactions, the optically-excited fullerenes transfer energy from their long-lived metastable triplet states to molecular oxygen, thus forming singlet oxygen with high yields [13].

ESR revealed that, in contrast to C_{60} and C_{70}, under illumination with white light, the lanthanum metallo-fullerene, La@C_{82}, did not produce singlet oxygen. While using ESR, we also checked the photocatalytic properties of La@C_{82} towards the photo-decomposition of a stable nitroxide radical, 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO), and found no marked photocatalytic activity of this metallo-fullerene. However, from a substantial loss of the ESR signal of La@C_{82} in these experiments (~25%), we inferred formation of the light-induced diamagnetic forms of La@C_{82}.

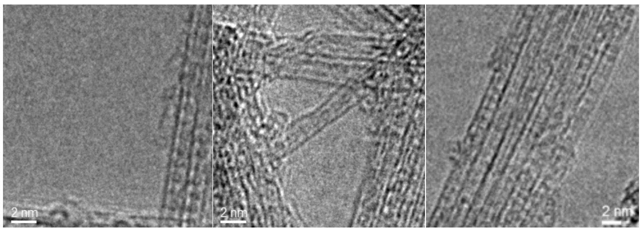

Figure 1 Illustration of high filling in SWNTs with fullerene content.

2 Experimental

SWCNTs with the average diameter of ~1.4 nm were produced using laser ablation technique in the presence of non-magnetic catalysts Pt:Rh:Re. SWNTs were purified using a combined oxidation and microwave digestion steps [14]. We were provided with 35μM concentration of La@C_{82} in CS_2. Pure C_{60} fullerenes (99.5%) from Bucky USA were used as separating molecules for the spin-active La@C_{82} in peapods. Therefore, before encapsulation of SWCNTs, La@C_{82} in the stock solution was diluted with C_{60} in the following proportions: 1:100, 1:20, 1:10, and 1:1, thus resulting in 1, 5, 100 and 100% relative content of La@C_{82} in the peapod filling.

Before encapsulation, the ends of SWCNTs were opened by oxidation in fixed air at 350 °C for 20 min. Then, SWNTs were coated with an appropriate combination of mixed fullerenes, by dropping and drying out the prepared solutions on the nanotube sample. Prepared sample is sealed under vacuum in a quartz tube. To ensure the encapsulation process, the C_{60}/La@C_{82} coated SWCNTs were annealed in vacuum for 4 days at 450 °C. ESR experiments on peapods in the temperature range of 5-300 K were performed using an X-band Bruker ESR spectrometer (EleXsys 540) equipped with a high-Q cylindrical cavity.

The ESR assay of the photo-catalytic properties of La@C_{82} in CS_2 was performed at room temperature using an X-band Bruker ESP 300E spectrometer equipped with a standard TE102 cavity. To measure the generation efficiency of $^1\Delta_g$, the stock CS_2 solutions containing 35 μM concentrations of either C_{60}, C_{70} or La@C_{82} and 25 mM concentration of a singlet oxygen-scavenging reagent, 2,2,6,6-tetramethyl-piperidine (TMP), from Sigma, were equilibrated with air. The diamagnetic substrate, TMP, reacts with singlet oxygen, which yields an ESR-detectable product, TEMPO. This approach, firstly introduced by Lion *et al.* [15], is thought to be highly specific to the formation of singlet oxygen [16].

Then, aliquots of *ca.* 70 μL were transferred into 2.0 mm ID and 2.4 mm OD quartz capillary tubes from VitroCom, NJ, USA (sample height of 25 mm). The quartz capillaries containing either of the prepared solutions were exposed to the white light from a halogen source (150 W halogen lamp) outside the ESR cavity at the stabilized temperature of 21 ± 1 °C.

3 Results and discussion Single-wall carbon nanotubes (SWCNTs) produced by laser ablation with the use of non-magnetic catalyst, Pt:Rh:Re, have been found more suitable for preparing the prospective spin-active peapods as compared to those obtainedby using standard magnetic catalysts [17]. In particular, effective removal of the local magnetic fields related to the remnant magnetic catalysts promotes longer spin-coherence times in prospective qubits. High resolution TEM imaging was used for preliminary evaluation of the obtained peapods. Representative TEM images of C_{60}/La@C_{82}-filled peapods are shown in Fig. 1. The images demonstrate a high level of filling of SWCNTs with the fullerene species. Further TEM investigations will be made to investigate the distribution of the endohedral fullerenes in the peapods [18], to determine how effectively the empty C_{60} cages 'dilute', and thus separate, the La@C82 molecules. ESR characterization of the magnetic properties of C_{60}/La@C_{82}-filled peapods was performed for peapods with the relative content of La@C_{82} of 1, 5, 10, and 100%. For all the measured samples, the experimentally observed line-shapes could be deconvoluted into two major components, *i.e.* narrow and broad Lorentzian lines. The example of the deconvolution these two components and a simulative fit of the ESR spectrum of peapods containing 1% of La@C_{82} is shown in Fig. 2. The linewidth of the narrow component slightly increases upon doping, remaining less than 1G, except for 100% case. For the broad component this tendency for broadening with the doping level was even more pronounced (Fig. 3). The ESR-derived spin susceptibility obtained by numerical double integration the broad ESR component revealed the similar behavior to that previously reported for pristine carbon nanotubes, *i.e.* 'super-Curie' increase below 50 K and `Curie-type` above 50 K [19].

As can be seen in Figure 4, with increasing relative content of La@C_{82} in peapopds, a shift of the resonance field of the broad component towards higher magnetic fields was observed.

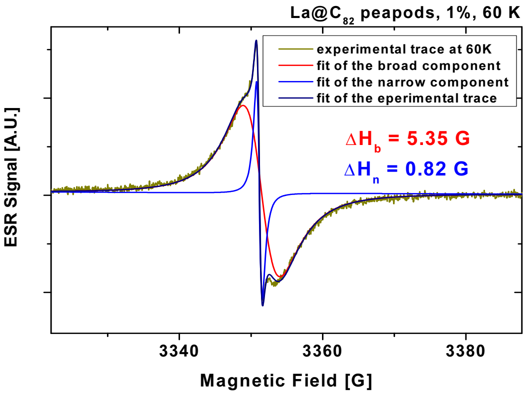

Figure 2 The ESR trace acquired at 60 K for peapods having the relative La@C_{82} content of 1%. The simulative fit and deconvolution into narrow and broad components are also shown.

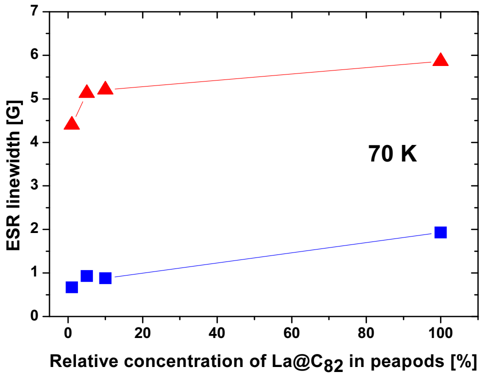

Figure 3 Line width evolution of the narrow (full blue squares) and broad (full red triangles) components of the ESR spectrum as a function of the relative La@C82 content in peapods.

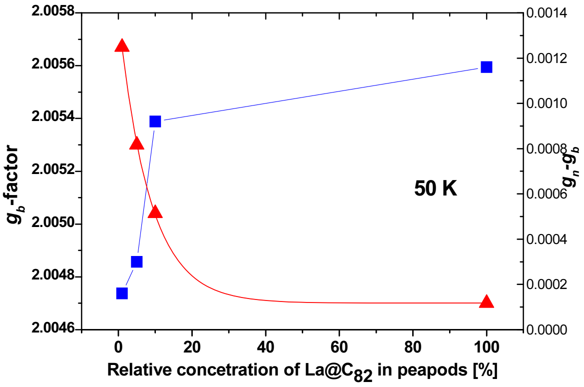

Figure 4 Evolution of g_b-factor of the broad ESR component as a function of the relative content of La@C_{82} in peapods (red full triangles). The relative g-factor shift for the broad and narrow ESR components, g_n-g_b, as a function of of the relative content of La@C_{82} in peapods (blue full squares).

At temperatures below 70 K, the g_b-factor of the broad component decays rapidly with increasing relative content of La@C_{82}. Interestingly, however, this tendency changes to the opposite one at temperatures higher than 70 K (data not shown).

Since the characteristic redox and photo-catalytical properties of La@C_{82} are significantly different from those of the empty fullerene C_{82}, as well as from pristine C_{60} and C_{70}, we also performed preliminary studies of its photophysical properties in CS_2. Firstly, we checked the ability of La@C_{82} to photosensitize singlet oxygen under illumination with white light. The results of singlet oxygen scavenging in this experiment are shown in Fig. 5. In this approach, the growing ESR signal of TEMPO as a function of illumination time is proportional to the amount of the photo-sensitized singlet oxygen. The ESR reactive scavenging in the presence of La@C_{82} under illumination with visible light did not reveal formation of any measurable

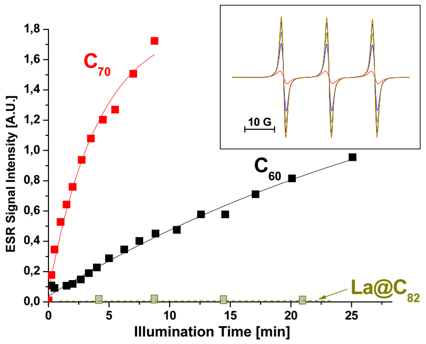

Figure 5 ESR reactive scavenging of singlet oxygen ($^1\Delta_g$) photo-produced in the presence of either C$_{70}$, C$_{60}$ or La@C$_{82}$. CS$_2$ solutions containing 25 mM TMP and 34.6 μM concentrations of either C$_{70}$, C$_{60}$ or La@C$_{82}$ were illuminated with visible light (halogen lamp). Inset**:** representative ESR traces showing the growth of the ESR signal of TEMPO as a function of illumination time.

amounts of $^1\Delta_g$. This result is in good agreement with theoretical predictions of Tagmatarchis *et al.* for an active spin doublet located on the C$_{82}$ cage [20]. In contrast, as can be seen in Fig. 5, both C$_{60}$ and C$_{70}$ efficiently sensitized the formation of $^1\Delta_g$. The observed marked difference in slopes of the kinetic plots for C$_{60}$ and C$_{70}$ has been observed previously in other solvents, including toluene [21], and is customarily associated with a considerably larger oxygen quenching rate constant for C$_{70}$ than that of C$_{60}$ [22]. While using ESR, we also checked the photocatalytic properties of La@C$_{82}$ towards decomposition of a stable free radical, TEMPO. The time courses of the photo-decomposition of TEMPO under illumination with visible light in the presence of C$_{70}$, C$_{60}$ or La@C$_{82}$ are shown in Fig. 6. The fastest decay rate of TEMPO was observed in the solution containing C$_{60}$. The linear semi-logarithmic plot of TEMPO decay versus illumination time points to the exponential character of this process (inset to Fig. 6). In the presence of La@C$_{82}$, the photo-decomposition of TEMPO was found considerably slower and occurred with almost the same rate as in the control experiment in the absence of any photocatalysts (control I in Fig. 6). It is worth noting that in the dark and in the absence of any photocatalysts TEMPO remained entirely stable over a prolonged period of time (control II in Fig. 6).

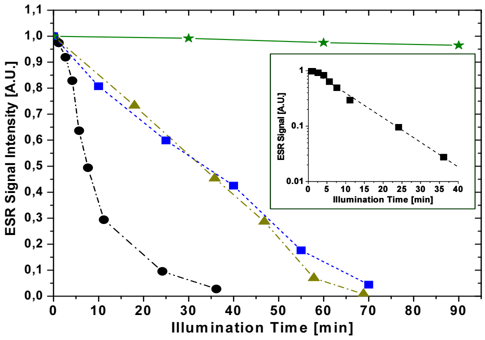

Figure 6 Photo-decomposition of 50 μM TEMPO in CS$_2$ solutions containing 34.6 μM concentrations either of C$_{70}$, C$_{60}$ or La@C$_{82}$ under illumination with visible light (halogen lamp). Black full circles: solution of 34.6 μM C$_{60}$ and 50 μM TEMPO in CS$_2$ under visible light illumination. Blue squares: solution of 50 μM TEMPO in CS$_2$ under VIS illumination (control I); dark yellow triangles: solution of 34.6 μM La@C$_{82}$ and 50 μM TEMPO in CS$_2$ under illumination; olive stars: solution of 50 μM TEMPO 50 mM in the dark (control II). Inset: semi-logarithmic plot of the time course of the photo-decomposition of TEMPO in the presence of C$_{60}$.

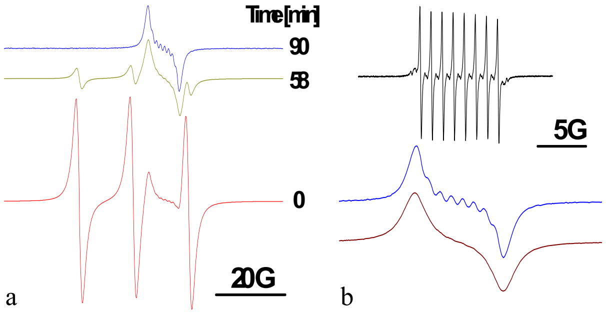

Figure 7 (a) Representative ESR traces acquired during the photo-decomposition of TEMPO in the presence of La@C$_{82}$. CS$_2$ solution containing 50 μM TEMPO and 34.6 μM concentration of La@C$_{82}$ was illuminated with visible light (halogen lamp). (b) Room temperature ESR spectra of La@C$_{82}$ acquired for: air-equilibrated CS$_2$ solution (bottom), after 90 min of illumination of CS$_2$ solution of La@C$_{82}$ and TEMPO (final phase of the photo-decompostion of TEMPO) (middle), and for the degassed solution of La@C$_{82}$ in CS$_2$ (top).

The representative spectra showing evolution of the ESR signals observed during illumination with visible light of CS$_2$ solutions containing both La@C$_{82}$ and TEMPO are shown in Fig. 7a. At the beginning of the process, the characteristic ESR spectrum of TEMPO consisting of three equidistant peaks is strongly distorted since it overlaps with features belonging to La@C$_{82}$. The hyperfine structure in the latter spectrum is not resolved since the experiment was started using a non deoxygenated solvent (CS$_2$). As can be seen in Fig. 7a, during the photo-decomposition of TEMPO, its three ESR peaks disappearwith time, whereas the ESR spectrum of La@C$_{82}$ is becoming progressively more marked. Interestingly, the emerging ESR spectrum of La@C$_{82}$ also slightly evolves. In particular, the hyperfine structure is better resolved for longer illumination times. For better clarity, three ESR spectra acquired for air-equilibrated, partially degassed, and nominally deoxygenated solutions of La@C$_{82}$ in CS$_2$ are shown in juxtaposition in Fig. 7b.

Although in the above measurements we did not observe directly any photocatalytic activity of La@C_{82}, the experiment involving illumination with visible light the CS_2 solutions containing TEMPO and La@C_{82} revealed a drop in La@C_{82} concentration of ~25%. This substantial loss of the spin-active lanthanum endohedral fullerene can be associated to the formation of diamagnetic anionic ([La@C_{82}]$^{-1}$) or cationic ([La@C_{82}]$^{+1}$) forms.

On the other hand, the observed resolution improvement of the La@C_{82} hyperfine structure with illumination time can be assigned to several factors, including: (i) consumption and concentration diminishment of the dissolved oxygen, (ii) progressive reduction of TEMPO (spin-relaxant), and (iii) progressive concentration diminishment of the spin-active La@C_{82} itself (~25% loss after 70 min of illumination).

4 Conclusions Spin-active endohedral fullerenes, La@C_{82}, were successfully encapsulated in magnetic catalysts-free SWCNTs. TEM images indicate a high level of filling in the obtained peapods, while ESR measurements confirm the presence of La@C_{82}.

The observed changes in the ESR features, *i.e.* linewidth broadening and shift of the resonance fields upon increasing La@C_{82} content, suggested the presence of spin-active La@C_{82} molecules in obtained peapods.

It has already been demonstrated that the characteristic redox properties of La@C_{82} are significantly different from those of the empty fullerene C_{82}, as well as of C_{60} and C_{70} [23]. In particular, the formation of stable diamagnetic forms of La@C_{82} in chemical and electrochemical processes has been reported [10]. It has also been well established that La@C_{82} is a stronger electron donor and acceptor as compared to the empty fullerene [24]. In this context, our observation of the light-mediated spin-silencing of La@C_{82} in CS_2 solutions is interesting since it sets the stage for further investigations of the light-induced formation of diamagnetic forms of endohedral metallo-fullerenes, including more complex constructs, such as peapods filled with spin-active metallo-fullerenes.

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