Preparation and stabilization of C₆₀-carbon nanotube exohedral hybrids with controlled nano-morphology

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Abstract

Molecularly engineered non-covalent hybrids comprising carbon nanotubes (CNTs) and fullerenes may combine the electronic and mechanical properties of CNTs with the optical and excellent electron acceptor characteristics of the fullerenes. As was demonstrated by us in a previous study, a two-step process comprising solution processing of multi-wall nanotubes (MWNTs) followed by vacuum deposition of fullerenes can be used for the preparation of non-covalent C₆₀-MWNTs hybrids. Transmission electron microscopy measurements and Raman characterization indicate that the hybrids comprise random 3D scaffolds of individual MWNTs and fullerite nanocrystals. While surface migration of the fullerenes on the MWNTs surface leads to coarsening of the nanocrystals, we find that controlled induction of SP³ point defects on the MWNTs surface (via UV/O₃ treatment) traps the initial nano-morphology and preserves the nano-dimensions and structure of the fullerene crystals. The nano-morphology of the treated nanotubes is preserved also when the hybrid is coated by a polymer layer (poly(3-hexylthiophene-2,5-diyl), P3HT, and the polymer-hybrid films show significant quenching of the photoluminescence, indicating that these hybrids could be useful in photovoltaic applications where the typical size of the nano-domains and the degree of crystallinity of the fullerenes play an important role in light-matter interactions.

Graphical abstract

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s42452-019-0483-7>) contains supplementary material, which is available to authorized users.

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SN Applied Sciences (2019) 1:473 | <https://doi.org/10.1007/s42452-019-0483-7>

Received: 23 February 2019 / Accepted: 11 April 2019 / Published online: 19 April 2019

Keywords Carbon nanotube · Fullerenes · Exohedral hybrids

1 Introduction

Molecularly engineered hybrids comprising carbon nanotubes (CNTs) and fullerenes may combine the electronic and mechanical properties of CNTs with the optical and excellent electron acceptor characteristics of the fullerenes [1]. In *endohedral* C₆₀-CNTs hybrids, the fullerenes are enclosed within the CNT forming the so-called carbon nanopeapod (C₆₀@CNT) in which interactions between the fullerenes and the CNT are of van der Waals (vdW) type [2]. As for *exohedral* hybrids, covalently linked structures including nanobuds [3, 4], and fullerenes linked to functionalized nanotubes were reported [5–7]. Stable vdW-type *exohedral* fullerene-CNTs assemblies have not been reported yet, probably due to the strong segregation tendencies of the pristine nanostructures: The fullerenes tend to form micron-sized crystals, and the CNTs form bundles [1]. However, it was theoretically predicted that C₆₀ fullerenes may organize into monolayers on CNTs, forming a carbonaceous *core-shell* vdW hybrid [8]. Semi-empirical and molecular dynamics calculations revealed that structural defects in the nanotubes can promote the formation of such hybrids as they increase the adhesion of the fullerenes to the CNTs [9]. Fullerene-CNTs vdW hybrids would constitute an optimal photoactive component for organic photovoltaics (OPV) devices: The fullerenes would induce efficient charge separation, and the CNTs networks, formed at low percolation threshold, would set high-mobility pathways for electron transport and effective nucleating agents for the photoactive polymers [10–12].

Recently, we reported [13] the preparation of all-carbon (C₆₀-CNT) exohedral vdW hybrids. The hybrids comprise 3D scaffolds of multi-walled CNTs (MWNTs) and nanocrystals of C₆₀ fullerenes. The typical diameter of the fullerite nanocrystals is 50–100 nm, and the inter-crystallite spacing is 60–100 nm (center-to-center distance). The process is based on a two-step sequence. First, pristine CNTs are deposited from liquid dispersion onto a target substrate and random 3D scaffolds of individual tubes assemble as the solvent is rapidly evaporated. In the second step, fullerenes are sublimated and deposited from the vapor phase onto the pre-assembled scaffolds [13]. In this system, structural defects and junction points in the MWNTs scaffolds were observed to act as nucleation points for fullerite nanocrystals. In the present paper, we investigate the stability of the hybrids. In particular, we observe that post-deposition annealing (at temperatures of up to 95 °C) and aging at room temperature result in surface migration of fullerenes along the CNTs, leading to reorganization

and coarsening of the fullerene domains. We suggest and demonstrate that the initial nano-morphology, and in particular the dimensions of the nano-sized fullerene crystals, may be preserved by deliberate induction of sp³ nano-domains on the outer shells of the MWNTs. The defects prevent surface reorganization by serving as barriers for surface migration of the fullerenes, and do not affect the photovoltaic activity of the fullerenes as indicated by photoluminescence measurements (quenching of the intensity) of P3HT-C₆₀-CNTs hybrids.

2 Experimental details

2.1 Materials

MWNTs-Arkema (Arkema Inc. USA <http://www.arkema.com/en/>) of average diameter 10–15 nm and typical length of 10 μm and MWNTs-MER (MER corporation, Tucson, AZ USA <http://mercorp.com/nano.pdf>) of average diameter 25–45 nm were used. Chloroform was purchased from Sigma, ortho-dichlorobenzene (odCB) from Acros Organics. Poly(3-hexylthiophene-2,5 diyl), P3HT, Mw 58,000 gr/mol, polydispersity index = 2.0, from Rieke Metals.

Lacey electron microscopy (TEM) grids (01883-F Lacey F/C 3000 mesh Cu, TEDPELLA INC) were stripped from the carbonaceous coating using chloroform. The stripped grids were exposed to plasma cleaning (PLASMA CLEANER PDC-32G) for 20 s and gold-coated by sputtering (EMITECH K576X, Emitech Ltd, England) to a final thickness of few nanometers.

Quartz slides (Lianyungang Lanno Quartz Co., Ltd, china) were cleaned by sonication in ethanol and acetone.

Mica substrates (SPI Supplies, USA, 12001-26-2) were freshly cleaved.

2.2 Preparation of C₆₀-MWNTs hybrids

Step 1: Solution assembly of 3D MWNTs scaffolds was carried out by deposition of CNTs from ortho-dichlorobenzene (odCB) dispersions following sonication (50 W, 43 kHz) at 0 °C of non-treated CNTs powders at concentrations ranging between 0.001 and 0.1 wt%, in accordance with a previously published procedure [13]. The scaffolds were deposited on gold-coated TEM grids, quartz substrates and mica. Fast evaporation of the solvent resulted in the formation of quenched random 3D scaffolds. The characteristic mesh size of the scaffolds is determined by the flexibility of the CNTs (characteristic persistence length, L_p, of the tubes [14]). As is seen in the TEM images (Fig. 1) the MWNTs are flexible (L_p < 100 nm) and form scaffolds with a broad distribution of mesh sizes between 250

and 500 nm. Note that the TEM images (Fig. 1a, b) present a 2D image of the 3D scaffolds, where network cells are overlaid one on top of the other. The SEM image (Fig. 1c) shows more clearly the 3D nature of the scaffold.

UVOCS ultra-violet ozone cleaning systems, T10X10/OES UVOCS INC, USA ozone content 1–4 ppm (270 min), were used for induction of sp^3 nano-domains on the outer shells of the MWNTs.

Step 2: Direct deposition of C_{60} fullerenes from the vapor phase onto the solution assembled 3D scaffolds was carried out at sublimation temperature of 550 °C, rates of ~ 0.3 – $2 \text{ \AA/s}$ and substrate temperatures of 25 °C, 150 °C, 180 °C and 200 °C. The process was described in details in ref [15]. Deposition rate was monitored in situ by a quartz micro-balance (QCM). The exposure time was calibrated to the time required for the growth of a contentious layer of 10, 20 and 80 nm for each deposition rate (for 0.2° A/s this corresponds to 50 s, 100 s, and 400 s).

2.3 Characterization methods

TEM imaging was carried out using FEI Tecnai 12 G2 TEM equipped with a Gatan 794 CCD camera and operated at 120 kV.

Raman scattering: Horiba LabRam HR evolution micro-Raman system, equipped with a Synapse Open Electrode CCD detector air-cooled to -60°C was used. Excitation was induced by 532 nm, air-cooled frequency-doubled Nd:YAG laser (0.5 mW). The laser was focused by a $\times 100$ objective to a spot of about $1 \text{ }\mu\text{m}$. The measurements were taken with a 600 mm^{-1} grating and a $100 \text{ }\mu\text{m}$ confocal microscope hole. As the spectra of the C_{60} -MWNT hybrids were found to be affected by the exposure time (Fig. 2S in the ESM), similar exposure time of 30 s was used in all the reported measurements.

3 Results and discussion

3.1 Nano-morphology and Raman spectra of as-prepared C_{60} -MWNT hybrids

Typical nanocrystal diameter, inter-crystallite distance and the structure of fullerene nanocrystals deposited on MWNTs scaffolds were investigated via TEM imaging and electron diffraction. Figure 2 presents typical TEM images of as-prepared C_{60} -MWNTs hybrids. Electron diffraction of the fullerene clusters confirmed their *fcc* crystalline structure [13]. Statistical analysis of ~ 100 TEM images (Fig. 3) indicates that for a given deposition time (100 s) and deposition rate ($0.2 \text{ \AA/s}$), the median of the C_{60} crystal size distribution is 45 nm for substrate temperature of 25 °C and 26 nm for 180 °C (Fig. 3a). At a given substrate temperature and deposition rate, the typical center-to-center distance of the nanocrystals (Fig. 3b) becomes smaller with exposure time suggesting that under these conditions the process is controlled by nucleation of nanocrystals (rather than by crystal growth).

Statistical analysis of TEM images of more than 500 nanocrystals deposited on MWNTs scaffolds (Figure S1 in the ESM) indicates that most of the crystallites are grown at defect points or MWNTs junctions, in accordance with previous observations [13].

Raman spectra show C_{60} peak at $\sim 1466 \text{ cm}^{-1}$ and $< 8 \text{ cm}^{-1}$ shifts of the MWNT D and G bands to higher wavenumbers (in comparison with pristine MWNTs). The I_D/I_G ratio is not modified as compared to the un-coated MWNTs scaffolds (Figure S2 in the ESM) [16–18].

Fig. 1 TEM images of MWNTs scaffolds **a** MWNTs-MER, **b** MWNTs-Arkema, **c** SEM image of MWNTs-MER

Fig. 2 TEM images of as-prepared C_{60} -MWNTs hybrids at C_{60} (deposition rate of $0.2 \text{ \AA/s}$) substrate temperature 25°C (**a, b**) and 150°C (**c, d**)

3.2 The effect of thermal annealing on the nano-morphology of the hybrid

To test the morphological stability of the hybrids, the samples were annealed at 60°C , 80°C , 95°C under nitrogen atmosphere. Following the annealing, TEM characterization was carried out.

TEM images (Fig. 4) reveal that thermal annealing leads to migration of fullerenes from the nanocrystals along the MWNTs surface. After 1 h of annealing, one can observe the formation of thin C_{60} layer coating the MWNTs surface (Fig. 4b, c). Longer annealing results in reorganization into large C_{60} crystals (Fig. 4d). This process is illustrated in Fig. 4e and characterized statistically in Fig. 5. Indeed, the population of small and medium-sized crystallites

(< 60 nm) is reduced by annealing, while coarsening leads to increased population of crystallites with a typical diameter > 85 nm (Fig. 5a), along with the expected increase in the center-to-center distance of the larger nanocrystals (Fig. 5b). Similar reorganization of C_{60} fullerenes was observed in samples incubated at ambient conditions for 2–3 weeks.

Nanocrystals coarsening upon annealing or aging reduces the overall surface free energy of the hybrids, and thus presents a (thermodynamic) driving force for morphological reorganization of the fullerenes. In this system, C_{60} -MWNTs and C_{60} - C_{60} interactions are similar, vdW type; and thus, the barrier for fullerene migration along the CNTs surface is minor. Thus, fullerenes reorganization can be observed already at room temperature. To the best of our

Fig. 3 Statistical analysis of TEM images of C_{60} nanocrystals carried via “ImageJ” program. **a** Typical size distribution (here, deposition rate of 0.2 Å/s for 100 s) substrate temperature 25 °C (red) and

180 °C (blue). **b** center-to-center distance of C_{60} nanocrystals (here grown at a deposition rate of 0.2 Å/s, substrate temperature 25 °C 50 s (green) and 100 s (purple))

knowledge, this is the first report of surface migration of C_{60} molecules on CNTs surfaces, while a similar effect was reported at the C_{60} –graphene interface [19]. It should be also noted that control studies of C_{60} crystallites deposited onto mica and quartz substrates (Figure S3 in the ESM) did not reveal migration of fullerenes during post-deposition annealing (at room temperatures and temperatures of 80–95 °C). This suggests that the interaction of C_{60} molecules with graphene and CNTs is weaker than that with quartz or mica, where the growth of highly crystalline C_{60} films was reported before [20].

While the observed migration of C_{60} molecules over the CNTs surface is an interesting phenomenon, it presents a hurdle for application of the C_{60} –CNTs hybrids in OPV systems. Thus, in the next stage of the study we developed a method for stabilization of the nano-morphology of the hybrids.

3.3 Utilization of induced surface defects for prevention of surface migration of fullerenes

We hypothesized that induction of sp^3 defects at the MWNTs surface may introduce a barrier for fullerenes migration and reduce post-deposition coarsening upon thermal annealing. To test this hypothesis, we exposed the MWNTs scaffolds to ultra-violet light/ozone (UV/ O_3) treatment. It is well known that the CNTs react with ozone molecules in a carboxylation reaction leading to the formation of C=O, O–H and C–O and COOH functional groups, characterized by sp^3 hybridization of the MWNTs carbon atoms, and hydrophilic nature [21]. To identify the nature of the induced defects and quantify their concentration, we used Raman measurements [16, 17, 22–24]. The Raman

spectra of pristine MWNTs comprise three clear peaks (Fig. 6a): the G band, a double resonance D band, and the G' double and triple resonances band (see also Figure S2 in the ESM) [25]. While the D band is a forbidden transition for ideal non-defected graphene layers, it is permitted in the presence of structural defects that modify the sp^2 hybridization of the graphene layers and induce symmetry breaking [25–27]. The intensity of the D band, I_D , is proportional to the concentration of sp^3 defects, while the intensity of the G band, I_G , is almost not affected. Therefore, the I_D/I_G ratio (the *defect index*) provides a measure of the concentration of sp^3 defects and the average inter-defect distance [16–18]. Raman spectra of UV/ O_3 treated MWNTs–MER networks are presented in Fig. 6a. The dependence of I_D/I_G ratio on the exposure time to UV/ O_3 treatment is presented in Fig. 6b, showing that the low I_D/I_G ratio of the pristine MWNTs increases due to the UV/ O_3 treatment (see also Table S1 in the ESM).

The treated scaffolds were used for preparation of hybrids, and two sets of experiments were carried out. In the first, C_{60} –MWNT hybrids were annealed at 80 °C under nitrogen atmosphere. In the second, different samples were aged at ambient conditions for 5 months. The nano-morphology of the resulting hybrids was analyzed using TEM imaging (Figure S5 in the ESM and Fig. 7).

As can be seen from the TEM images (Figure S5 in the ESM) and statistical analysis (Fig. 7), pre-treatment of the MWNTs scaffolds by UV/ O_3 considerably improved the morphological stability of the hybrids: No C_{60} coarsening was observed after annealing or prolonged (5 months) aging at ambient conditions. We suggest that the hydrophilic nature of the carboxylate C=O, O–H and C–O and COOH functional groups induced by oxidation can form a barrier for fullerene migration along the MWNTs.

Fig. 4 Typical TEM images of C_{60} -MWNTs hybrids (**a**) as prepared (**b**, **c**) after 1 h of annealing at 80 °C (**d**) after 2 h of annealing at 80 °C (**e**) schematics presenting morphological rearrangement

Though preparation and characterization of functional devices based on the C_{60} -MWNT hybrids is beyond the scope of this study, we carried out preliminary experiments in which poly(3-hexylthiophene) (P3HT) was deposited onto the hybrids, similar to P3HT-fullerene blends used in polymer-based OPV devices [28]. The nano-morphology of the P3HT-coated $UV\text{O}_3$ -treated C_{60} -MWNT hybrids was investigated via TEM imaging (Figure S5 in the ESM). Statistical analysis of the images (Figure S6 in the ESM) reveals similar behavior to that of non-coated hybrids, indicating that $UV\text{O}_3$ treatment

stabilizes the nano-morphology of the hybrids also in the presence of P3HT coatings, very different from fullerene coarsening and segregation, commonly observed in P3HT-fullerene blends [29–31]. Measurements of the UV-Vis absorption and Photoluminescence (PL) of P3HT-hybrid thin films (Figure S8 in the ESI) show the expected quenching of the PL intensity due to well-known charge transfer between a conjugated polymer and C_{60} [29]. This indicates that the MWNTs-supported fullerene nanocrystals are photoactive. Further detailed investigation of the

Fig. 5 The effect of annealing at 80 °C on C₆₀-MWNTs hybrids **a** diameter distribution and **b** center-to-center distance of C₆₀ nanocrystals. As-prepared hybrids (blue) 1 h of annealing (red) 2 h of annealing (green)

Fig. 6 **a** Raman scattering spectra of untreated MWNTs (red) and after 270 min of exposure to UV/O₃, **b** the effect of exposure time on the I/I_G ratio. The dashed line is a guide to the eye

hybrids' electronic properties is required before they could be used in various functional devices, including solar cells.

4 Conclusions

Thermal sublimation of C₆₀ fullerenes onto 3D scaffolds of MWNTs was shown to result in the assembly of exohedral vdW (non-covalent) hybrids comprising MWNTs and fullerenes nanocrystals with a typical *fcc* structure and tunable nano-morphology of the fullerenes nanocrystals [13]. It was found that the weak vdW interaction at the fullerene-MWNTs interface and the high surface energy of the nano-structured hybrids result in reorganization of

the C₆₀ nanocrystals into larger, micron-sized crystals, at a wide temperature range (25–80 °C). However, the nano-morphology of the fullerenes domains, the diameter and inter-nanocrystal distance can be preserved by induction of sp³ point defects at the surface of the MWNTs. These sp³ defects prevent migration of fullerenes along the MWNTs walls but do not affect charge transfer as indirectly indicated by the quenching of the PL in P3HT mixtures of the hybrid.

The two-step processing approach presented here enables the engineering of carbonaceous materials with tunable nano-morphology and may be utilized for the preparation of active layer in P3HT-fullerene layers for OPV applications.

Fig. 7 The effect of annealing at 80 °C (2 h, nitrogen) on the nano-morphology of UV/O₃-treated C₆₀-MWNT hybrids on the size distribution of fullerenes nanocrystals (**a**), and their center-to-center

distance (**b**) (The data were collected from 150 TEM images). As-prepared hybrids (blue) 1 h of annealing (red) 2 h of annealing (green)

Acknowledgements The authors acknowledge the support of the Israel Science Foundation (Grant no. 72/14). R. Y-R holds the Stanley D. and Nikki Waxberg professorial chair in Advanced Materials.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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