Solvent effect on morphology of pristine nanohorns

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Abstract
The morphological change of nanohorns aggregates is presented. Scanning electron microscope (SEM) analysis was conducted on a pristine sample and dispersions. Polar solvents (water and ethanol) were used and stored for one day and one week, observing different packing aggregates.

Introduction
A single-walled carbon nanohorn (SWCNH or NH) is an allotrope form of carbon. It is made of a cone shape (20–40 nm length, 5 nm widths) with a definite apex composed by pentagons [1] [2] [3]. The pristine nanohorns powder shows a tendency to assembly into spherical-like aggregates, often named Dahlia flower or bud-like. These structures appear as large as 70–100 nm diameter from a sonicated dispersion. However, when the morphology of the pristine dry powder (without sonication) is observed, larger spherical aggregates are found.

Objective
To observe whether the morphology of assembled nanohorns is affected by ageing and solvent.
Solvent effect on morphology of pristine nanohorns

As Received

H2O (1 Day)

H2O (1 Week)

EtOH (1 Day)
Figure Legend

Figure 1. SEM Images of Pristine Nanohorn.

(A) Dry NH.
(B) NH stored for 1 day in water.
(C) NH stored for 1 week in water.
(D) NH stored for 1 day in ethanol.
(E) NH stored for 1 week in ethanol.

Materials
Nanohorns powder was purchased from Carbonium S.r.l.

Preparation and Characterisation
The NH powder was dried at 150ºC in an oven to prevent gas or water adsorption, and then was stored in a desiccator. All the dispersions were prepared using a single powder batch and freshly prepared with a nominal concentration of 2 mg/mL. In practice, 8 mg of NH were dispersed in 4 mL of solvent and homogenised for 3 min by means of a vortex. Before being used, all dispersions are set for 2–3 h up to equilibrium. In the next step, each dispersion was dried in an oven at 150ºC until a dry powder is obtained (3–4 h).

Morphology of nanohorns were recorded by means of a scanning electron microscope (SEM, Philips XL30 TMP, 20KV) on the dry powders.

Results & Discussion

Figure 1A shows the commercial nanohorn, carried out using SEM analysis. This material is made into spherical or ellipsoidal clusters exhibiting a size distribution of 5–20 μm. The dimension of the NH aggregates appear to be larger by about two orders of magnitude compared to the values reported from other authors (~100 nm) by means of TEM analysis [4] [5]. To date, we have found only one publication that reports a SEM image for pristine NH, Cioffi and coworkers [6]. In the consulted literature, sample preparation comprises a sonication step to allow a homogenous dispersion. To avoid a possible alteration of the NH aggregates, in our experiments we limit the high-energy treatment by mixing all samples manually. In order to observe the effect of a polar solvent on the assembling character, we dispersed NH in distilled water and ethanol and stored up to 1 week.

In figure 1B, an aqueous dispersion, stored for 1 day, shows NH assembly into spherical aggregates with average sizes 5–15 μm. By keeping the dispersion for 1 week, the average size of the spherical aggregates is increased up to 10–30 μm (as seen in Fig. 1C). On the other hand, the solvent substitution with ethanol produces parallelepiped-like aggregates, as seen in figure 1D1 and E1. It is worth noting that the top side of the parallelepiped aggregate appears to be composed of a cluster of spherical aggregates possessing an average size in the range 5–10 μm (Fig. 1D3, E3). By contrast, the bulk of this parallelepiped-like aggregate turns into a layered structure, as observed in figures 1D2 and E2. We posit that the solvent influences the size of the spherical aggregates, which are reduced when the polarity of the solvent is changed. The morphology of nanohorns can be explained by a parallelism with surfactants. These classes of materials exhibit the formation of spherical aggregates, micelles, that spontaneously assemble, minimising the van der Waals interactions. Eventually, surfactants will form compact structures (liquid crystals). Similarly, nanohorns assemble into a complex and hierarchical structure that determines its packing assembly character.
Conclusions
In conclusion, we observe a larger spherical aggregates for pristine NH. The use of distinctive polar solvents changes the interaction between NH units, leading to the formation of a distinct structure. So far, spherical morphology turns to generate more compact crystalline-like structure.

Additional Information

Methods
Materials
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Supplementary Material
Please see https://sciencematters.io/articles/201606000009.

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Ethics Statement
Not applicable.

Citations


