MoS_2 and WS_2 Inorganic fullerenes and nanoboxes synthesized by spray pyrolysis

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Since the discovery of the inorganic fullerene-like particles (IF) and nanotubes of lamellar compounds by Tenne and co-workers[i], many routes have been investigated for their synthesis. IF and nanotube metal dichalcogenides (MX_2, with M = Mo, W, and X = S, Se) have been widely studied because their ability to form nested structures was discovered in the first place. It was early found that they exhibit better tribological properties than their bulk counterparts[ii]. Various methods have been successfully used for their synthesis, as for example: conversion of metal oxides under H_2X atmosphere[iii], decomposition of ammonium tetrathiometallates at high temperature (nanotubes only)[iv] or by sono(electro)chemistry (IF only)[v], laser ablation of MoS_2[vi], microwave plasma with metal chloride or carbonyl and H_2S or $SeCl_4$ as precursors[vii], arc discharge with a Mo-MoS_2 powder anode submerged in DI water[viii].

Until now, only the first process has been developed for the production of IF MoS_2 and nanotubes in large quantities, which however uses the highly toxic H_2S gas. Hence, new synthesis routes more friendly with the environment are still needed. Ideally, they should have a large number of adjustable parameters to control the IF morphologies, allow the use of several types of precursors, and be compatible with mass production process (high yield and rate).

Here, we present a new route based on spray pyrolysis at high temperature of aqueous or ethanolic solutions of ammonium tetrathio-metallates, which fulfill most of these requirements. Preliminary results show that IF-MoS_2 and WS_2 can be reliably produced. We found that several parameters involved in liquid spray pyrolysis have a strong influence on the morphology, either direct like the droplet size, or indirect like the nature of the solvent, which actually results in the occurrence of new MX_2 nested structures.

Synthesis of IF-MoS_2. MoS_2 particles obtained by spray pyrolysis of $(NH_4)_2MoS_4$ solutions exhibit a spherical shape irrespective of the nature of the solvent (water or ethanol). The size of the particles obtained from aqueous solutions is distributed over two different values (~ 450 and ~ 100 nm in diameter), as it is classically observed with a pneumatic spray. Sprays of ethanolic solutions lead to a more uniform size distribution (around ~ 300 nm), although fullerenes with different sizes can also be obtained (Fig. 1).

Synthesis of IF-WS_2. IF-WS_2 with the same morphology (spherical shape) than that of IF-MoS_2 are obtained by spray pyrolysis of $(NH_4)_2WS_4$ aqueous solutions. In contrast, spraying ethanolic solutions does not exclusively lead to IF-WS_2 particles with a spherical morphology. Some WS_2 particles (a few percents) can adopt an original type of nested structure, exhibiting the shape of a parallelepiped, with multilayer walls and an empty core, thus describing a "closed nanobox" (figure 2). The size of these rectangular WS_2 particles ranges from ten to a few hundred of nm. Noteworthy, most of them exhibit the same length/width ratio, ~ 1.9, irrespective of their size. The influence of parameters such as the droplet size, the nature of the solvent, or the temperature, on the IFs' morphology will be presented and discussed.

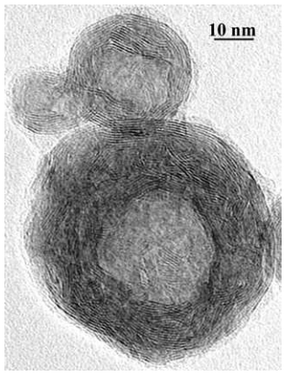

Fig. 1 MoS_2 Fullerene

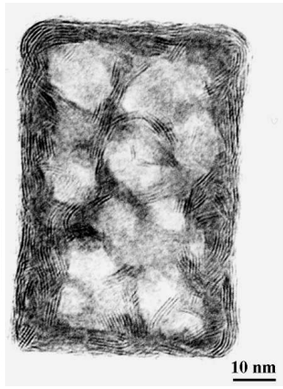

Fig. 2 WS_2 nanobox

In conclusion, spray pyrolysis is a relatively simple and well-known technique offering a large number of adjustable parameters to tailor the morphology of MS_2 IF. The formation of an original nested structure consisting in a closed nanobox of WS_2 demonstrates the potential of this technique. This method may also provide an "easy way" to test the ability of other inorganic lamellar compounds to form IF and is potentially suitable for the implementation of an industrial process.

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