Encapsulation of WC within 2H-WS_2 inorganic fullerene-like cages

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The preparation of WC encapsulated within 2H-WS_2 inorganic fullerene-like (IF) cages by sulfidisation is described; the encapsulates were prepared from both high surface area (high S_g) and low surface area (low S_g) WC precursors; for low S_g WC, partial conversion of the carbide to the sulfide only was achieved with 2–20 IF layers obtained around carbide particles, resulting in WC/2H-WS_2 composites; the amount of conversion obtained in the case of the high S_g WC depended on the method of preparation of the precursor; total conversion to 2H-WS_2 was obtained from a precursor obtained by carburisation of small WO_3 particles, while only partial conversion was obtained in the instance of high S_g WC prepared from ball-milled low S_g WC.

Inorganic fullerene-related structures (IFs) of the form 2H-MX_2 with M = W, Mo and X = S, Se can be prepared by a variety of routes including gas–solid[1–4] and vapour phase[5] reaction between a sulfidising agent and a metal oxide, by STM induction from amorphous MoS_3 films[6] and also by chemical-transport reactions.[7] Such materials owe their fullerene-like properties to the fact that they can incorporate non-six membered moieties that result in the formation of both curved and closed multiple layered structures similar to those formed by graphitic carbon.[8] These materials have found uses in tribological applications[9] and also in nanoscale electronic devices.[10] We describe here the encapsulation of 2H-WS_2 IF material around particles of the corresponding monocarbide. This result is novel as WC is a much denser and more metallic material than the oxide or sulfide precursors previously used to synthesize IFs.

The low S_g WC used in these experiments exhibited average particle sizes of 0.3–2.5 μm and was obtained from Alfa Chemicals (99.5%). The high S_g WC was prepared by two methods. First, WC (α-form) with a surface area of 40 $m^2\ g^{-1}$ and particle diameters in the range 200–2000 Å was prepared by reacting WO_3 with a mixture of 20% CH_4–H_2 (100 ml min^{-1}), ramping the temperature from 20 to 750 °C at the rate of 1 °C min^{-1}.[11] The carburisation of this precursor was verified in the bulk by X-ray powder diffraction (XRD) using a Philips 1729 diffractometer equipped with Cu-Kα_1 radiation operated at 40 kV and 30 mA. The second high S_g sample was prepared by grinding the commercially available low S_g WC in a ball milling apparatus for 48 h. This technique also produced a precursor with particle sizes in the range 200–2000 Å. All of the sulfidisations were carried out in a standard flow reactor at a temperature of 820 °C using a mixture of forming gas (5% H_2–95% N_2) at 110 ml min^{-1} and H_2S at a flow rate of 4 ml min^{-1}. All precursors and their resulting encapsulates were characterised by electron diffraction (ED) and high resolution transmission electron microscopy (HRTEM).

In general, IFs prepared from the low S_g (*i.e.* large particle size) WC precursor materials were completely covered by the encapsulating 2H-WS_2 network which varied from between 2 and 20 2H-WS_2 layers per encapsulate. The size of the resulting encapsulates were found to be in the same range as the precursor particles (see above), although some slight expansion in size had probably occurred as a result of the conversion from the relatively dense carbide to the much bulkier sulfide [Fig. 1(a)]. For these relatively large encapsulates, there was no obvious crystallographic relationship between the hexagonal $P\bar{6}m2$ WC structure [Fig. 1(a)] and the encapsulating $P6_3/mmc$ 2H-WS_2 network [Fig. 1(a)]. In Fig. 1(b), for example, is shown a large carbide encapsulate (denoted **WC**) coated with a non-uniform 2H-WS_2 'skin', the external form of which was determined by the adventitious morphology of the precursor rather than by the encapsulate microstructure. On the surface of the encapsulate in Fig. 1(b), a small 2H-WS_2 nanotube (denoted **N**) has formed on the surface of the encapsulate that presumably originated from an asperity occurring on the surface of the unreacted WC precursor. A further point is that, regardless of the length of the sulfidisation step, the 2H-WS_2 material did not penetrate beyond a depth of *ca.* 100 Å into the WC encapsulates, except where assisted by surface irregularities of the type giving rise to the prominent feature in Fig. 1(b).

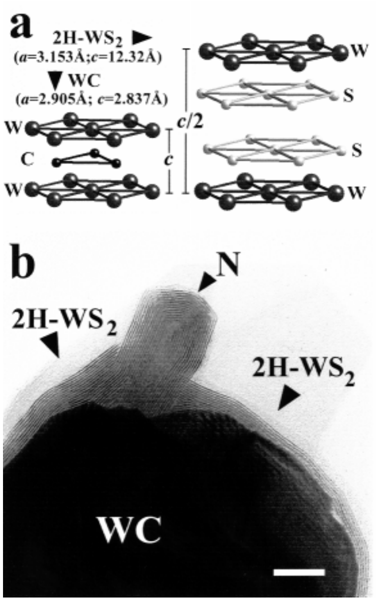

Fig. 1 (a) Schematic depictions of the hexagonal $P\bar{6}m2$ WC and $P6_3/mmc$ 2H-WS_2 structures showing the differences in *c vs.* stacking. (b) HRTEM micrograph showing 2H-WS_2 encapsulated low S_g WC particle. A small asperity in the original precursor particle has led to the formation of a small nanotube (**N**) on the surface of the encapsulate (scale bar ≈ 140 Å).

In the instance of encapsulates formed from the high S_g WC originating from carburised WO_3, near complete conversion to 2H-WS_2 IF structures was achieved. In the example shown in Fig. 2(a), a completely reacted and ellipsoidal 2H-WS_2 structure (overlapping with other IF material) is visible. A 'C'-shaped shard of IF material (denoted **S**) is also visible in the lower left region of the micrograph. Even in structures originating from relatively larger precursor particles than those giving rise to the structures in Fig. 2(a), fully reacted IFs were generally obtained.

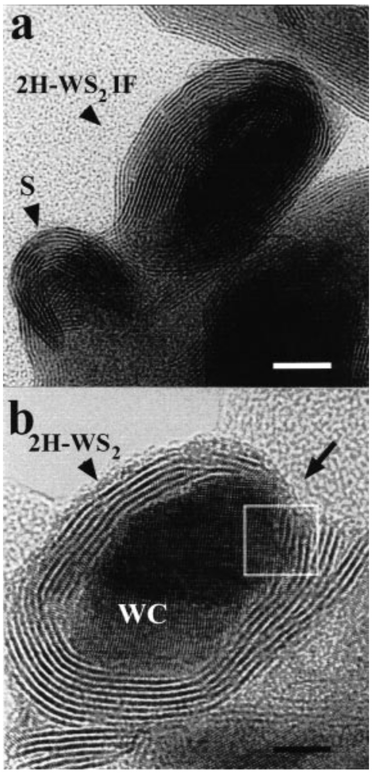

Fig. 2 (a) HRTEM micrograph showing a 2H-WS$_2$ IF nanoparticle originating from a high S_g precursor formed by carburisation of small WO$_3$ particles. A small C-shaped shard (**S**) of IF material is visible in the lower left of the micrograph (scale bar ≈ 75 Å). (b) 2H-WS$_2$ IF encapsulated high S_g particle formed from a ball milled WC precursor (scale bar ≈ 50 Å).

This total conversion can be explained in terms of fairly high residual oxygen content present in the carburised precursor, which may be either present in the main bulk of the WC particles as oxycarbide or on the surfaces of the carbide particles as an oxidised passivated layer.

The main difference between IF materials grown from the precursor originating from the carburised WO$_3$ particles and the ball-milled WC precursor is that the latter product still contained unreacted carbide. Furthermore, as with encapsulates formed from the low S_g (*i.e.* large particle size) WC precursor, the number of encapsulating shells formed around the encapsulate was limited to 2–20 regardless of the length of the sulfidisation step. In Fig. 2(b), we see a small carbide encapsulate formed from a ball milled WC particle encased in a 2H-WS$_2$ IF 'shell' of variable thickness up to 10 layers. Note that in the upper right region of the micrograph, a small break in the coverage is visible (arrowed) but the 2H-WS$_2$ coverage of most of the observed encapsulates was generally found to be complete. These smaller encapsulates yielded information with respect to the growth mechanism of the encapsulating sulfide material from the carbide. In Fig. 3(a) we see a fast Fourier transform (FFT) calculated from the WC/2H-WS$_2$ interface obtained from the region indicated by the superimposed square in Fig. 2(b). The main calculated reflections in the FFT can be indexed according to an $[01\bar{1}0]$ projection of WC. Superimposed upon the pattern, a blurred reflection corresponding to the (0002) planes of encapsulating 2H-WS$_2$ is visible. Note that this reflection is aligned along the [0001] direction with respect to the carbide. In Fig. 3(b) the microstructure of the carbide (denoted **WC**) in relation to the encapsulating sulfide (denoted **2H-WS$_2$**) is shown. A small disordered region of carbide (denoted **DS**) is visible at the lower middle of the micrograph caused either by mechanical deformation of the carbide during the ball-milling process or by stacking faults present in the original material. In a further enlargement [Fig. 3(c)], we see that two distorted layers of the carbide (denoted **WC**) intergrow with one layer (denoted **2H**) of the sulfide. This type of growth may be important in terms of initiating the propagation of the 2H-WS$_2$ encapsulating material. However, we see from the lower magnification micrographs of both the low S_g and high S_g WC encapsulates [*i.e.* Fig. 1(b) and 2(b)] that the adventitious morphology of the precursor plays a more important rôle in terms of determining the overall shape of the obtained encapsulates. This is in accordance with the previous observations for WO$_{3-x}$ oxides encapsulated within 2H-WS$_2$ IF materials.[12]

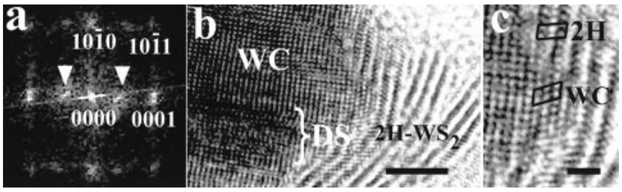

Fig. 3 (a) Calculated ED pattern, obtained from a FFT of the indicated region in Fig. 2(b) corresponding to the WC/2H-WS$_2$ interface. The 0002 reflections of the sulfide are arranged along [0001] with respect to the carbide. (b) HRTEM micrograph showing the WC/2H-WS$_2$ interface. A distorted region (**DS**) is visible in the carbide microstructure (scale bar ≈ 35 Å). (c) Enlargement of the WC/2H-WS$_2$ interface showing intergrowth between two layers of the distorted carbide structure (**WC**) and one layer of the sulfide (**2H**; scale bar ≈ 10 Å).

The consequence of encapsulation of WC inside 2H-WS$_2$ IF shells with respect to the composite physical properties will be to enhance considerably the structural rigidity of the resulting 2H-WS$_2$/WC encapsulates, which may enhance their performance in tribological applications. This would be an interesting result as WC is one of the hardest known materials. Furthermore, the inclusion of the more metallic metal carbide within the sulfide should also enhance the conductive properties of the resulting composite material.

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