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Study of the hydrostatic pressure dependence of the Raman spectrum of W/WS_2 fullerene-like nanosphere with core–shell structure

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Abstract

The structural behavior of a W/WS_2 fullerene-like nanosphere with a core–shell structure has been studied in the hydrostatic pressure range from atmospheric pressure to 18 GPa by Raman spectroscopy using a methanol–ethanol–water mixture (16:3:1) as the pressure transmitting medium (PTM). We found that it is interesting that the intensity ratio of the LA + TA mode and the A_{1g} mode changes with increasing pressure. We attribute this change to the shape transformation of an inorganic fullerene-like IF-W/WS_2 nanosphere under high hydrostatic pressure. By comparing the Raman spectra of an IF-W/WS_2 nanosphere released from high pressure with that of the original one, we found that the change in morphology is reversible. This indicates that the spherical shape of the IF-W/WS_2 has excellent behavior in resisting compression.

1. Introduction

Tungsten disulfide (WS_2) has an anisotropic layered structure, which is characterized by strong covalent bonds between the atoms within the molecular layer and weak van der Waals (vdW) forces between the layers. The structural anisotropy of this material has shown wide applications, such as photovoltaic solar cells [1], solid lubricants [2], battery cathodes and hydride sulfurization catalysis etc [3]. As a solid-state lubricant, WS_2 inorganic fullerene-like (IF-WS_2) nanoparticles show superior tribological performance over traditional platelet crystal analogues, and a low coefficient of friction and a low rate of wear, especially under high loads [4]. However, the changes in the crystal structure and shape of WS_2 under high hydrostatic pressure have not been studied widely, which is helpful in explaining the excellent compression-resisting behavior of WS_2 in the frictional process. To the best of our knowledge,

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only two reports have been published in the literature. Joly-Pottu *et al* found that the exfoliation of fullerenes may be caused by uniaxial pressure even without imposed shear, other than that generated by simple contact, by comparing the behavior of IF-WS_2 nanoparticles under high hydrostatic pressure with a Hertzian contact [5], and Rafailov *et al* calculated the axial and circumferential strains from the linearly shifting coefficients of the main two Raman modes with normalized pressure [6].

Raman scattering is known to be sensitive to small changes occurring in crystal structure. In this paper, we investigate the structural behavior of an IF-W/WS_2 nanosphere with a core–shell structure under high hydrostatic pressure using Raman spectroscopy. An interesting result has been found—the intensity ratio of the LA + TA mode and the A_{1g} mode changes distinctly with increasing pressure. We attribute this change in the ratio to the transformation in shape of an IF-W/WS_2 nanosphere under high hydrostatic pressure. By comparing the Raman spectra of an IF-W/WS_2 nanosphere released from high pressure with that of the original one, it is found that the change in morphology is reversible. This indicates that the spherical shape of IF-W/WS_2 has excellent compression-resisting behavior.

2. Experiments

An IF-W/WS_2 nanosphere with a core–shell structure was synthesized by the reaction of tungsten nanosphere and sulfur at relatively low temperatures (380–600 °C) under a hydrogen atmosphere. A tungsten nanosphere was prepared using the wire electrical explosion method [7].

In situ Raman measurements of an IF-W/WS_2 nanosphere with a core–shell structure under high pressure up to 18 GPa were carried out by using a diamond anvil cell (DAC). The sample was loaded in 100–150 μm diameter holes drilled in the T301 stainless-steel gasket. A methanol–ethanol–water mixture (16:3:1) was used as the PTM. The pressure at the sample was estimated using the standard ruby fluorescence technique. The Raman spectra of the samples were observed with a Renishaw inVia Raman Microscope, using a charge-coupled device (CCD) detector to collect the Raman scattered light. A laser beam from a He–Ne laser (633 nm wavelength) was focused inside the diamond anvil cell through a Leica microscope.

3. Results and discussion

A representative Raman spectrum for an IF-W/WS_2 nanosphere with a core–shell structure is shown in figure 1. Two dominant peaks are observed at 352 and 420 cm^{-1}, which are in agreement with those for a bulk sample of 2H-WS_2 [8]. The peak around 352 cm^{-1} is assigned to the E_{2g} mode for the motion of W–S atoms in the x–y layered plane, and the peak around 420 cm^{-1} is the A_{1g} mode for the motion of two S atoms along the z-axis of the unit cell.

It is noticed that a shoulder appears at lower wavenumbers of the Raman peak around 420 cm^{-1}, which is little observed in single-crystal WS_2 and a powder of bulk 2H-WS_2. The results of Gaussian fits are shown in the inset of figure 1. It is obvious that the Raman peak at around 420 cm^{-1} consists of two peaks: one appearing around 420 cm^{-1} and another appearing as a shoulder around 416 cm^{-1}. Based on the analysis of 2H-WS_2 single crystal by Sourisseau *et al*, the shoulder peak is attributed to two-phonon coupling originating from longitudinal acoustic (LA) and transverse acoustic (TA) phonons at the K-point of the Brillouin zone [9]. Chung *et al* have studied this mode in three kinds of bulk WS_2 [10]. A single crystal of WS_2 did not show such a peak, and the powder of WS_2 specimen exhibited a very small shoulder peak. However, they observed an obvious LA + TA mode in thin films of WS_2 grown on Si substrate. Furthermore, they compared the Raman spectra of the basal planes grown parallel to

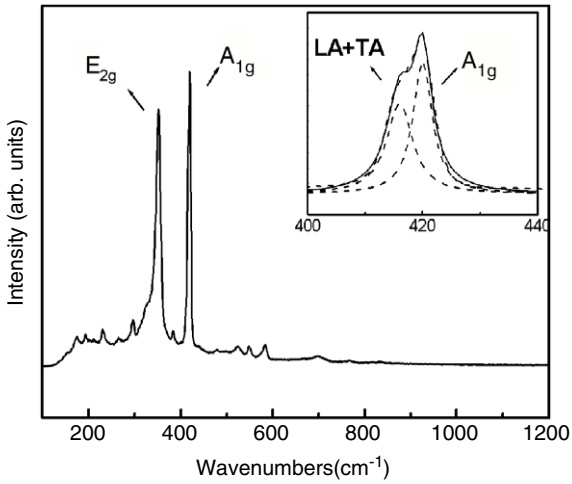

Figure 1. The Raman spectrum of an IF-W/WS_2 nanosphere with a core–shell structure at atmospheric pressure.

the substrate ($c(=)$) with those non-parallel to the substrate ($c(\|)$), and found that the relative concentration of the shoulder peak was increased when the fraction of $c(\|)$ became larger. Consequently, they considered that the occurrence of the localized curvature in a thin film seemed to be responsible for the enhancement of the LA + TA mode. Comparing the shape of our sample with the thin film that was studied, it is obvious that there is curvature in our sample. Thus we tentatively attribute the enhancement of the LA + TA mode to the curvature of the IF-W/WS_2 nanosphere. To prove this presumption, we further study the Raman spectra of the IF-W/WS_2 nanosphere under high hydrostatic pressure.

Raman spectra of the IF-W/WS_2 nanosphere under different pressures are shown in figure 2. It is clearly observed that the intensity ratio of the LA + TA mode and the A_{1g} mode changes noticeably with increasing pressure. This ratio first increases and then decreases, and finally almost stays constant, as shown in figure 3(a).

According to previous studies [11], we know that IF nanoparticles can retain their structure up to 25 GPa under shock-wave pressure. Thus we suppose that the structure of the IF-W/WS_2 nanosphere can survive up to 18 GPa in high hydrostatic pressure. From Chang's work, it has been determined that the shape of the pristine sample is a sphere or a quasi-sphere under ambient conditions. In fact, WS_2 has an anisotropic layered structure, which is characterized by strong covalent bonds within the molecular layer and weak van der Waals forces between the layers. So the c-direction of the layered structure is much more compressible than the other directions. We thus think that the effect of pressure on the sample is anisotropic, which induces the shape transformation of the sample even in quasi-hydrostatic pressure. The shape maybe first turns into an ellipsoid, then to an oblate sphere, and finally keeps it with increasing pressure, while a tungsten nanosphere is used as the core. Corresponding to this process, the curvature of the whole IF-W/WS_2 nanoparticle will first increase and then decrease, and finally almost stay constant. This is consistent with the change in ratio of the LA + TA mode and the A_{1g} mode. Therefore it is reasonable that the transformation in shape of a IF-W/WS_2 nanosphere under high hydrostatic pressure is responsible for this change in the intensity ratio.

A schematic illustration of the transformation in shape of an IF-W/WS_2 nanosphere with a core–shell structure under high pressure is shown in figure 3(b). The shape of the IF-

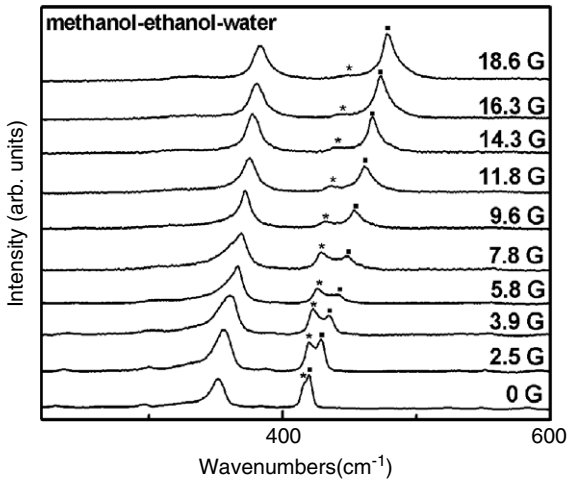

Figure 2. Raman spectra of the IF-W/WS_2 nanosphere with core–shell structure for various pressures at room temperature, recorded upon a pressure increase. The PTM is a 16:3:1 methanol–ethanol–water mixture. Asterisks and squares indicate the LA + TA mode and the A_{1g} mode, respectively.

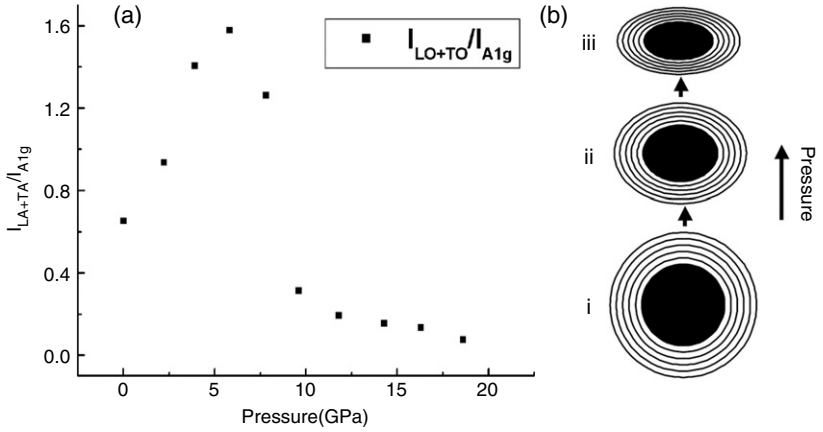

Figure 3. The pressure dependence of the intensity ratio of LA + TA mode and A_{1g} mode (a) and the shape transformation schematic illustration of IF-W/WS_2 nanosphere with increasing pressure (b) are shown.

W/WS_2 nanoparticle turns into an ellipsoid with increasing pressure in the low-pressure range of approximately 0–5.8 GPa (figure 3(b) ii). During this process, the curvature of the whole IF-W/WS_2 nanoparticle increases and arrives at a maximum up to 5.8 GPa. So, the intensity of the LA + TA mode is enhanced. The maximal ratio of the LA + TA mode and the A_{1g} mode is approximately 1.6 under a pressure of 5.8 GPa. With a further increase in pressure, the shape of the IF-W/WS_2 nanoparticle will turn into an oblate sphere (figure 3(b) iii), and the pressure range is approximately 5.8–11.8 GPa. In this pressure range, the curvature of the whole IF-W/WS_2 nanoparticle will decrease and the intensity of the LA + TA mode is weakened too. With higher pressure, the shape of the IF-W/WS_2 nanoparticle will not be changed distinctly. Only the distance between atoms decreases further. The pressure range is 11.8–18.6 GPa in

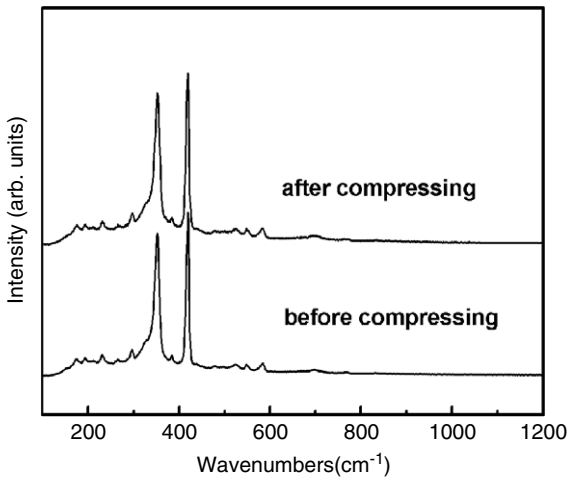

Figure 4. Raman spectra of the IF-W/WS_2 nanosphere with a core–shell structure at atmospheric pressure, and released from high pressure.

our experiment. The curvature of the whole IF-W/WS_2 nanoparticle barely changes, and the intensity ratio of the LA + TA mode and the A_{1g} mode stays almost constant.

We compare the Raman spectra of the IF-W/WS_2 nanosphere released from high pressure with that of the original one, and no evident change is observed (figure 4). This indicates that the change in morphology is reversible and that the spherical shape of the IF-W/WS_2 has excellent compression-resisting behavior.

4. Conclusion

In summary, the Raman study of an IF-W/WS_2 nanosphere with a core–shell structure has been carried out in the hydrostatic pressure range from atmospheric pressure up to 18 GPa. The intensity ratio of the LA + TA mode and the A_{1g} mode changes distinctly with increasing pressure. It first increases then decreases, and finally stays almost constant. We suggest that the transformation in shape of the IF-W/WS_2 nanosphere has been induced by high pressure, which is responsible for this change in the intensity ratio. A schematic illustration of the transformation in shape for an IF-W/WS_2 nanosphere with increasing pressure is presented. Also, it is found that the change in morphology is reversible, which indicates that the spherical shape of an IF-W/WS_2 has excellent compression-resisting behavior.

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