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A New Fullerene-like Inorganic Compound Fabricated by the Sonolysis of an Aqueous Solution of $TlCl_3$

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Abstract: The sonication of an aqueous solution of $TlCl_3$ under a flow of argon has led to a precipitate, which is composed of two products. The major product is Tl_2OCl_2, while Tl_2O is obtained in small quantities. The later has a structure of a multi-shell closed compound. The identification of the inorganic fullerenes in the TEM picture as the thallium(I) oxide is based on SAED measurements.

Introduction

Inorganic fullerene-like compounds were first described by Tenne and co-workers.[1] The nested fullerene-like compounds MX_2 (M = W, Mo; X = S, Se) were synthesized by a gas-phase reaction carried out at elevated temperatures.[1−3] The mechanism for the formation of these compounds and for their unique properties was also reported. Tenne has extended his studies and recently showed that cage structures and nanotubes exist also for $NiCl_2$.[4] The general trend as formulated by Tenne is that nanoparticles of layered compounds are inherently unstable in the planar form and adopt polyhedral (fullerene-like) topologies upon crystallization.[5] Other multi-shell closed inorganic structures include BN.[6] Almost all closed-shell compounds require high temperatures for their synthesis. The techniques by which these temperatures were achieved were furnaces,[1,3] laser vaporization,[8] arc discharge,[9] electron[10] and ion[11] beam heating, and the heating by an STM tip.[5] Suslick has synthesized a nanostructured MoS_2 by means of sonochemical methods,[12] and more recently we have demonstrated that fullerene-like MoS_2 can be prepared at room temperature by using sonoelectrochemistry.[13] Another synthesis of an inorganic fullerene (IF) which was carried out at low temperature (180° C) is that of VO_x.[7] In this contribution we report on the preparation of a closed multi-shell structure through the sonolysis of an aqueous solution of $TlCl_3$. Sonochemical reactions arise from acoustic cavitation phenomena: the formation, growth and collapse of bubbles in a liquid medium.[14] The extremely high temperatures (>5000 K), pressures (>20 MPa), and cooling rates ($>10^{10}$ K/s) attained during acoustic cavitation lead to many unique properties in the irradiated solution.[15] The sonochemistry of $GaCl_3$ has led to the formation of scroll-like cylindrical nanoparticles of gallium oxide hydroxide.[16] The sonohydrolysis of $InCl_3$ leads to the formation of bundles of noodle-like $In(OH)_3$.[17] The current report completes the sonohydrolysis measurements of group III A in the periodic table.

Unlike the sonication of carbonyls, which resulted in nanophase amorphous products,[18−20] the sonication of inorganic salts such as $GaCl_3$, $InCl_3$, or $TlCl_3$ yields crystalline nanophase products. The difference between the two reactions can be understood on the basis of the existence of two regions of sonochemical reactivity, as postulated by Suslick et al.: the inside of the collapsing bubble and the interface between the bubble and the liquid.[21] In the sonication of the transition-metal carbonyls, the reaction takes place inside the collapsing bubble, and the amorphous product is a result of the high cooling rates ($>10^{10}$ K/s) obtained during this collapse. In addition to the reaction in the gas phase that takes place within the collapsing bubble,

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Figure 1. TEM image of the as-prepared powder. Scale: 1 cm = 9 nm.

a reaction occurs in the thin liquid layer immediately surrounding the collapsing cavity.[21] For this reason, in the current reaction, the reaction takes place in the interfacial region as a result of the low volatility of $TlCl_3$.

Experimental Section

A solution of 1 g of $TlCl_3$ (Aldrich) in 50 mL of distilled water was sonicated for 1 h under a stream of argon at ambient temperature. The temperature was not controlled during the reaction and therefore reached 75 °C by the end of the reaction. The precipitate was washed three times by distilled water and centrifuged for 20 min. The pH was changed from 3.5 prior to the sonolysis to 2.8 after the reaction. As a control reaction the sonolysis of $TlCl_3$ was carried out in a closed cell at 350 °C for 2 h, and no sign of solid products was obtained.

Differential scanning calorimetry (DSC) of the dried product was carried out by using a Mettler DSC-30 with a heating rate of 10° C/min. The TGA measurements were carried out on a Mettler TGA-LG. The morphology of the product was determined by transmission electron microscopy (Philips CM-12) operating at 120 kV. Samples for TEM analysis were deposited onto carbon-coated copper grids (G-300 mesh). Electron diffraction patterns were generated at a camera length of 990 mm.

Results

A transmission electron microscopy (TEM) image of the as-prepared material is shown in Figure 1. The image depicts closed and nonclosed layered structures. About 40% of the as-prepared material had a closed structure. The closed crystalline layers (typically 15 to 20) are assigned to Tl_2O. The assignment is based on the measured interlayer distance of the closed crystalline layers (typically 15 to 20) which is 6.27 Å. This is assigned to the distance between adjacent layers ($c/6$) of Tl_2O. Further support for this assignment is obtained from other measurements. The layers can be clearly seen surrounding a featureless amorphous core. From the two-dimensional TEM picture, we cannot tell whether the particles are in the form of disks (or cylinders) or whether they are layered in all directions, like the inorganic fullerene-like structures. In Figure 2 parts a−c display TEM images of a single particle at different orientations with respect to the electron beam. The fact that the molecular layers are seen at different angles is a convincing demonstration of the curved and closed nature of the structures. If the sample were flat, as is normally the case for layered materials, an image of the layers would be seen only when the layers were aligned with the electron beam.

Table 1: Comparison between the Literature *d*-Spacing (Å) of Tl_2O and the XRD and SAED Results Measured for the As-prepared Material

d-spacing from XRD	*d*-spacing from SAED	Tl_2O “bulk” sample (JCPDS card no. 28-1320)
6.274	6.27	6.199 (006)
3.131	3.13	3.130 (0012)
2.987	2.98	2.993 (012)
2.875	2.89	2.890 (104)
2.812	2.81	2.825 (015)

The XRD diffraction pattern of the powder is presented in Figure 3a. The diffraction lines were assigned to Tl_2O (JCPDS card no. 28-1320) and to Tl_2OCl_2 (JCPDS card no. 37-543). The comparison between the measured *d*-values for the first six diffraction lines of Tl_2O and the literature values (JCPDS card 28-1320) is listed in Table 1. Tl_2O crystallizes in a monoclinic structure[22] with lattice parameters $a = 3.516$ Å $c = 37.84$ Å and $\beta = 120°$. The Tl_2O structure can be described as an anti-CdI_2 polytype, where the thallium atoms form a hexagonal close-packed layer sequence in which the oxygen atoms occupy alternate interlayer octahedral sites. Each Tl_2O layer consists of an oxygen layer sandwiched between two thallium layers and has six layers as a repeating unit. Strong covalent bonds hold the atoms within the layers, and the layers are stacked together by weak van der Waals forces.

The spacing between two adjacent layers in carbon nanotubes[23] and inorganic fullerenes[3] ($c/2$) is somewhat larger than that of the planar corresponding structures. The lattice expansion was ascribed to strain relief in the folded structure. A similar mechanism of strain relief is demonstrated for Tl_2O. Figure 3b shows the first X-ray diffraction peak of Tl_2O (006), which corresponds to the distance between adjacent layers ($c/6$). The peak position is shifted compared with that of bulk Tl_2O (vertical line) by an average of 1.5% along the c-axis. The average crystal size was calculated from the Debye−Scherrer formula to be 25 nm (also see Figure 1). The shape of the diffraction peak from the 002 plane is symmetric[24] in all previously reported IFs and symmetric in Tl_2O as well. On the other hand the diffractions from the 107 and 0012 planes reveal an asymmetry or even a shoulder to the higher 2θ values. These are related to the small size of the detected particles.

Selected area electron diffraction (SAED) of the multilayered structure shows a ring pattern corresponding to Tl_2O (Figure 2d). The SAED is obtained for the area shown in the TEM images (Figure 1). The SAED was performed with an aperture ($\Phi = 1.5 \mu$m). In this case, the electron diffraction is obtained from typically four to five layered structures of Tl_2O. The *d*-values calculated from the measured SAED are listed in Table 1 and compared with the literature values. To study the SAED of the core, a selected large closed structure was monitored. No electron diffraction pattern could be discerned, and high-resolution TEM of the core did not show a crystalline image.

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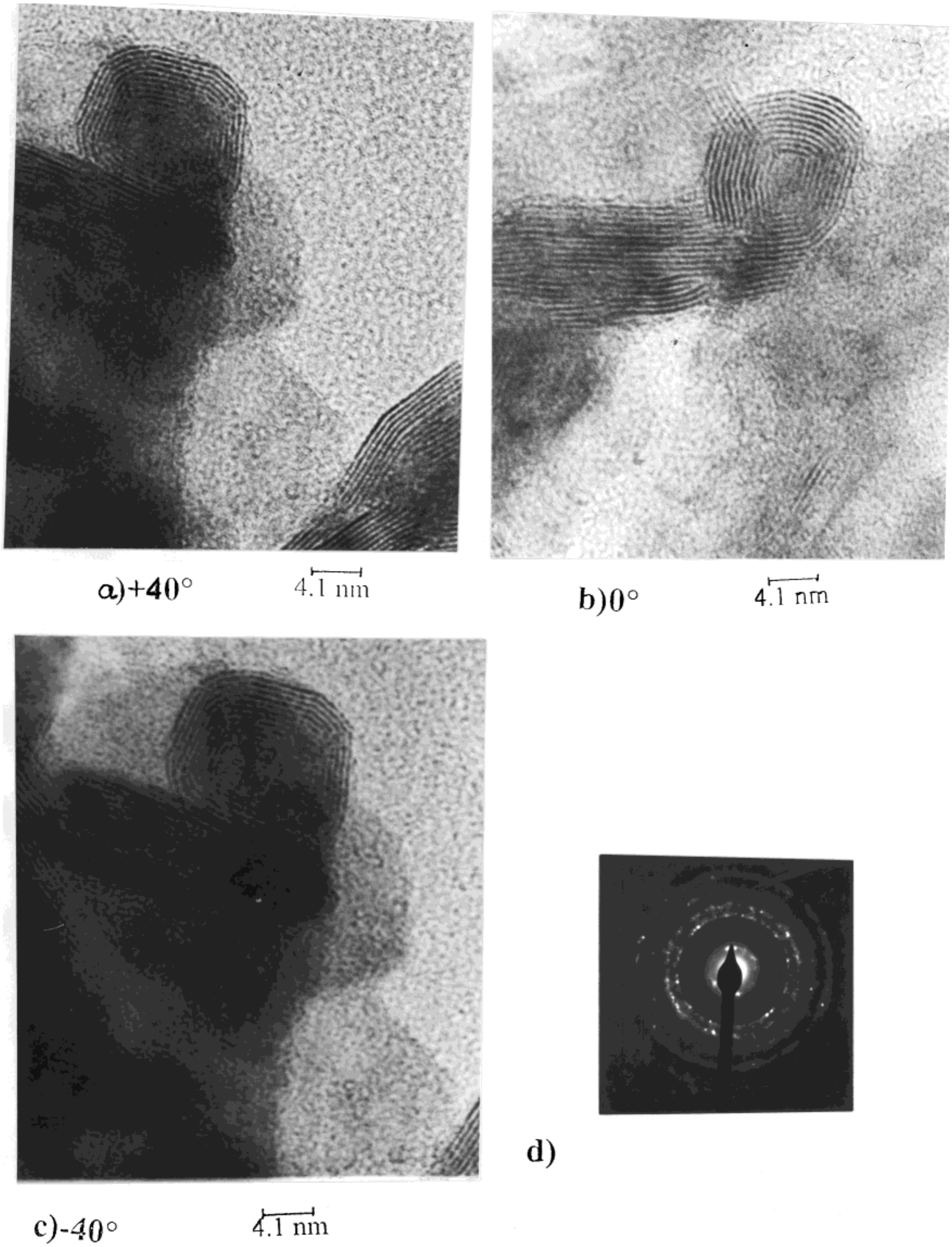

Figure 2. TEM image of the as-prepared powder at different tilt angles. (a) +40°, (b)0°, (c) −40°. Scale: 1 cm = 4.1 nm. (d) SAED inserted.

We do not know yet if the core of the fullerene-like structure is amorphous or hollow, and further investigations are now in process.

The TGA provided a quantitative estimate for the amount of the two products this is due to the fact that the TGA experiment showed that the as-prepared material lost 85−95% of its weight in the temperature range of 400−700° C. When the vapors of the powder were mass-analyzed at 400° C, a major peak at 510.993 amu, corresponding to $Tl_2OCl_2 \cdot H_2O$ (^{203}Tl) was observed. The isotope distribution of the observed peaks fits well with the calculated masses of the $Tl_2OCl_2 \cdot H_2O$. The vapor pressure of the Tl_2O in this temperature range is low,[25] and we have utilized this fact to enrich the mixture with the Tl_2O by heating the as-prepared mixture in a flow of argon. This enrichment of the IF is detected by TEM. The relative XRD peaks, of the Tl_2O in the annealed state (300° C in argon) are also enhanced. Previous studies[26] of the chemical stability of thallous compounds support our results and show that, when Tl_2OCl_2 was heated at temperature >250 °C, it started to decompose. The products of the decomposition were found to be chlorine, oxygen, and TlCl.

For both products, the reaction involves reduction of the Tl^{3+} ions to +1 and +2 oxidation states. These products are the

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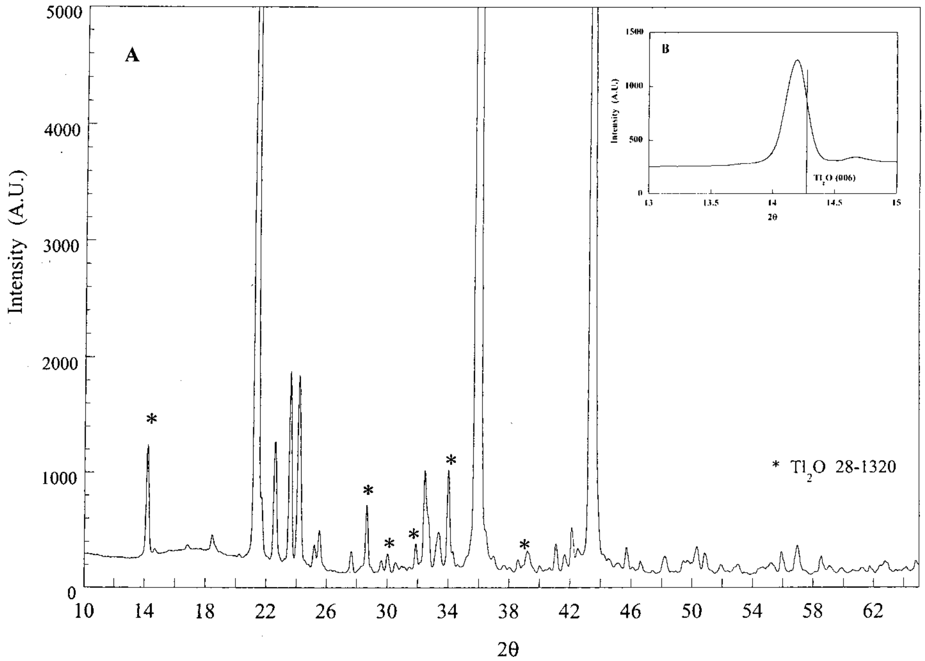

Figure 3. (i) XRD diffraction pattern of the as-prepared material. (ii) First diffraction peak of Tl_2O as compared with the bulk position.

results of the sonolysis of the water molecules to H and OH radicals, which occur in the gas phase during the collapse of the cavitational bubble. These radicals react with the Tl^{3+} ions in a small 200 nm ring surrounding the collapsing bubble:

$$Tl^{3+}{}_{(aq)} + H \rightarrow Tl^{2+}{}_{(aq)} + H^{+}{}_{(aq)} \qquad (1)$$

The Tl^{2+} is further reduced to Tl^{1+} by reacting simultaneously with a second H radical. We can eliminate however, the possibility of a one-step trimolecular reaction occurring by benefiting from the local high temperature that speeds up this slow reaction. In fact, the similar sonochemical reduction of Tl^{1+} yielding Tl^{0} has already been reported.[27] It is also worth mentioning that for the sonhydrolysis of $GaCl_3$ we have found that about 2% of the gallium atoms were reduced to metallic gallium.[16]

The growth mechanism of both carbon and inorganic fullerenes is not yet fully understood. However, it is believed that the main stimulus for the formation of fullerene-like structures emanates from the large energy associated with the dangling covalent bonds at the edges of the layered structures. The growth conditions of fullerene-like structures, in most cases, are far from equilibrium. The large thermal energies during growth force the nanoclusters of layered materials to close and form fullerene-like structures.

On the basis of the growth mechanism of the fullerene-like structures and the sonochemical reduction of the Tl^{3+} ions described above, we suggest the following mechanism to explain the formation of the closed curved structures. In the first stage, Tl_2O is formed via the sonochemical reduction of the Tl^{3+}. It is known that sonohydrolysis of aqueous solutions of metal ions is caused by the high local temperatures in or near the cavitation bubbles.[21] If the original Tl_2O particle is planar (two-dimensional), curvature and closure of the fullerene-like structures may occur around the collapsing bubble. The temperature gradient from the bubble surface into the solution should cause a temperature gradient across the particle that causes the curvature. This is helped by the energetics, which favors sheet closure due to bond energy released by eliminating reactive edges in the planar structures.

In conclusion, the sonochemistry of an aqueous solution of $TlCl_3$ induces crystallization of fullerene-like Tl_20 particles in ambient conditions. XRD and high-resolution TEM studies demonstrate the multilayered closed structure of the product. The sonochemical process provides a new method for the formation of closed structures at room temperature. This will probably be applicable to other layered compounds, and furthermore, experimental variables may allow control of particle size, shape, and size distribution.

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