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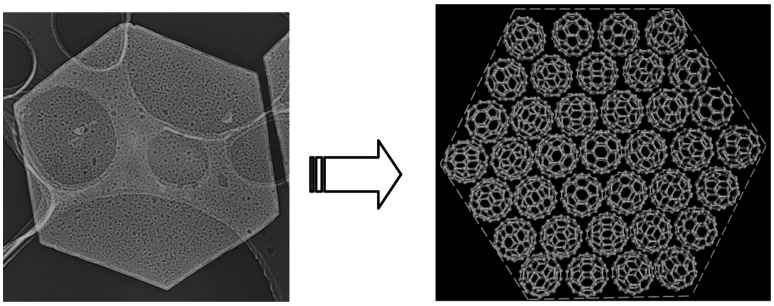

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Size-Tunable Hexagonal Fullerene (C_{60}) Nanosheets at the Liquid−Liquid Interface

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Fullerene (C_{60}) has gathered much attention in materials chemistry owing to their future potential application in various fields.[1] In general, solid C_{60} solvates have been prepared with various solvents by slow evaporation of solvents under slightly reduced pressure. The morphology for the C_{60} solvates has been tuned with disparate crystal structure in the solid state by changing the solvents. Basically, the nature of the solvent plays an imperative role on the crystal formation and its morphology and shape. Unusual crystal shapes with a few hundred micron size C_{60} solids have been observed when *n*-heptane, *n*-hexane, chloroform, benzene, toluene, and *m*-xylene, etc., were used as solvent.[2] Solid-state structural investigations on the hexagonal C_{60} haloform solvates with CCl_4, CH_3CCl_3, $BrCCl_3$, etc., were also reported in the literature with large size hexagonal crystals (>80 μm).[3] Furthermore, most of the C_{60} solvates are not stable in atmosphere, and it degrades rapidly when removed from the mother liquor.[3] Recent developments in the 1D nanostructured materials have rekindled the C_{60} nanostructures and its prospective applications. Recently, various attempts have been made to prepare stable crystalline C_{60} nanosize materials with various kinds of morphology such as nanorods,[4] nanotubes,[5] and nanowhiskers,[6] etc. Tuning the particle size to a desired range is one of the key factors in the nanotechnology. However, a facile route for the preparation of desired crystalline C_{60} solid with tunable particle size is under exploration.

Here we report a simple method for the preparation of size-tunable C_{60} hexagonal thin crystalline nanosheets via a liquid−liquid interfacial precipitation method. This method was introduced by our group for the preparation of C_{60} nanowhiskers at the toluene/isopropyl alcohol (IPA) interface.[6a] It has opened a new door in the preparation of C_{60} nanoparticles research and has been exploited for the preparation of various kinds of nanowhiskers. Very recently, we showed that this method was also effective for the preparation of porous C_{60} nanowhiskers.[7] In this work, for the first time, we report the preparation of very thin hexagonal crystalline C_{60} nanosheets at the carbon tetrachloride (CCl_4)/alcohol interface. Interestingly, the size of the hexagonal nanosheets could be tailored merely by changing the alcohol. A very large size (~7.5 μm diameter) hexagonal nanosheet was observed for the CCl_4/IPA interface, whereas the diameter of the hexagonal nanosheets decreased to ~2.5 μm and 500 nm at the CCl_4/ethanol and CCl_4/methanol interface, respectively. Irrespective of the alcohol, the thickness of the hexagonal nanosheets was almost uniform in size, and the nanosheets were transparent in nature. The sizes of the prepared hexagonal nanosheets were ~10 times smaller than the previously reported hexagonal C_{60}·CCl_4 solvates.[2b]

Figure 1 shows the scanning electron microscopic (SEM) image of hexagonal crystalline C_{60} nanosheets prepared at the CCl_4/IPA interface. These representative images show the hexagonal morphology of the C_{60} precipitate with highly transparent outlook. The observed particles were almost uniform in size (~8.9 μm in height and ~7.7 μm in diameter). The SEM images of CCl_4/EtOH and CCl_4/MeOH interface prepared hexagonal nanosheets are shown in Figure 2a,b and Figure 2c,d, respectively. Before the SEM measurements, the samples were dried at room temperature for 24 h.

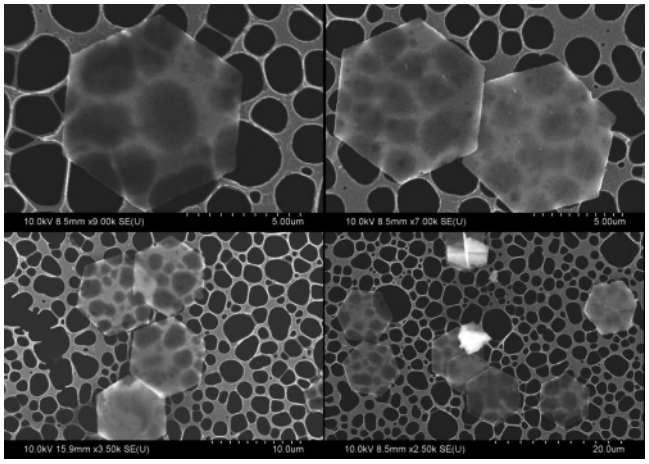

Figure 1. SEM images of hexagonal C_{60} nanosheets prepared at the CCl_4 and IPA interface.

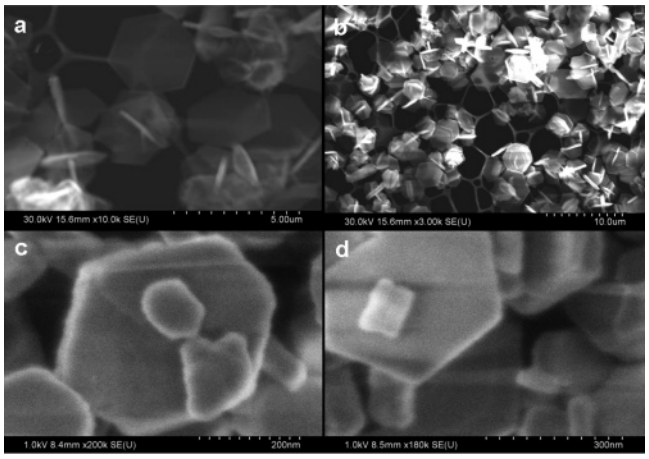

Figure 2. SEM images of C_{60} hexagonal nanosheets prepared at (a and b) the CCl_4 and EtOH and (c and d) the CCl_4 and MeOH interface.

The reason for the formation of hexagonal nanosheets with tunable size with the alcohol has not been clearly understood. However, it is speculated that the number of carbon atoms and the polarity of the alcohol plays a vital role on the particle size variation. The formation of hexagonal nanosheets was not observed for the higher chain length alcohol (*n*-butanol, 2-butanol, *n*-pentanol) in the studied experimental conditions, which indicates that the polarity of the alcohol should be high enough to form the hexagonal nanosheets.

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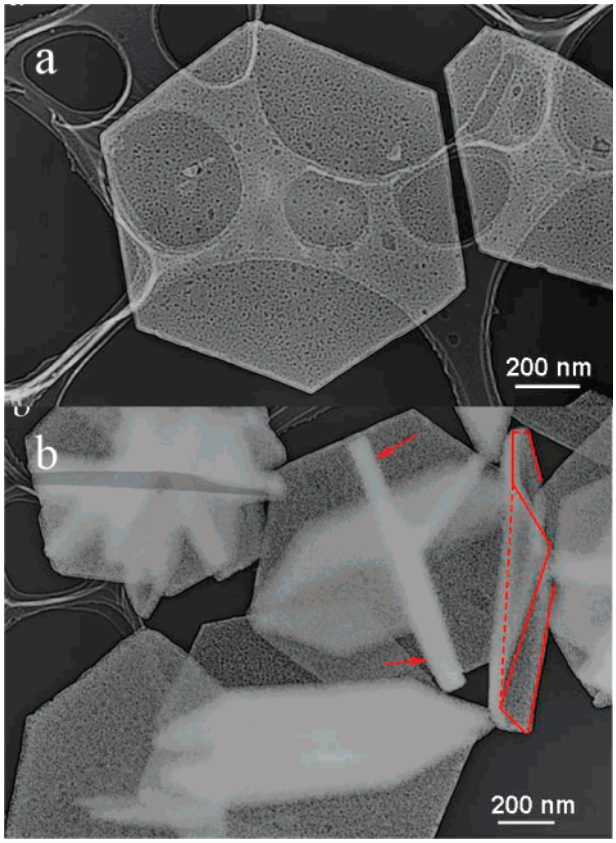

Figure 3. TEM images of C_{60} hexagonal nanosheets in the CCl_4 and ETOH interface.

Figure 3a shows a representative TEM image of the hexagonal nanosheets prepared at the CCl_4/EtOH interface. The observed hexagonal nanosheets were uniform in size for a particular CCl_4/alcohol interface. For instance, the CCl_4 interfaces with IPA, EtOH, and MeOH were 7−9 μm, 2−3 μm, and 500−700 nm, respectively (see Supporting Information). Further, the observed hexagonal nanosheets showed very fine pores over the entire nanosheets, irrespective of the nature of the alcohol. Similar observation of "traces of hexagonal channels" has been reported by Ceolin et al. with C_{60}·2(CH_3)CCl_3 solvate[8] with a size of >100 μm. Unlike the common C_{60} solvates, the observed hexagonal nanosheets were extremely stable in the air after they were removed from the mother liquor. Also, these nanosheets were highly transparent and flexible. The flexible nature of the nanosheets can be seen in Figure 3b; the red line indicates the inward fold of the hexagonal nanosheet, and the red arrows indicate a rolled hexagonal nanosheet. Presumably, these folded hexagonal nanosheets are highly thin and undergo this rolling effect in order to reduce the surface energy.

The inset of Figure 4 shows the selected area electron diffraction pattern (SAED) of the hexagonal nanosheets prepared at the CCl_4 and EtOH interface. The calculated *d* values corresponding to the (110) and (102) planes clearly indicate the presence of hexagonal crystalline structure. The X-ray diffraction (XRD) pattern of the hexagonal nanosheets prepared at the CCl_4 and alcohol interface revealed the existence of hexagonal crystalline nature. The calculated *d* values were in good agreement with the reported values of the hexagonal crystalline structure[9] with the lattice constant of $a = 10.250$ Å and $c = 10.719$ Å for all three samples. From the XRD studies, the formation of hexagonal crystalline structure was found to be favorable at the CCl_4 and alcohol interface. Further, the XRD results highlighted the vital role played by the nature of the alcohol in the formation of hexagonal nanosheets and its size.

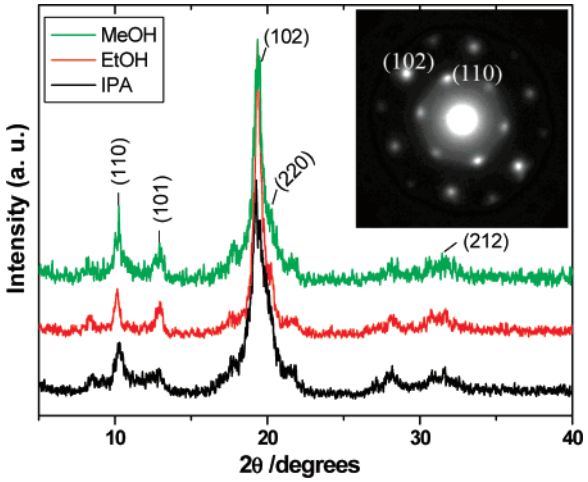

Figure 4. XRD patterns of C_{60} hexagonal nanosheets at different solvent interface. Inset: SAED pattern of the hexagonal nanosheets prepared at the CCl_4 and EtOH interface.

In conclusion, we synthesized hexagonal C_{60} nanosheets using a liquid−liquid interfacial precipitation method. The size of the hexagonal nanosheets can be tuned appropriately by selecting proper solvent for the interfacial precipitation. The synthesized hexagonal nanosheet opens a new platform for the fundamental studies, such as for bulk C_{60} solvates. In addition, the potential exploitation of these size tunable hexagonal nanosheets for various applications is awaiting.

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Supporting Information Available: Synthesis of hexagonal nanosheets and characterization procedure are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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