On Accretion of Nanosize Carbon Spheres

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In this paper, the high chemical activity of the newly synthesized nanosize carbon spheres is demonstrated. The carbon spheres can be accreted by a treatment in acetone. The mechanism for the accretion is attributed to the combination of the hydrogen and oxygen atoms belonging to the acetone molecules with the adsorbed hydrogen and/or oxygen atoms at the edges of the open graphitic flakes distributed at the surface of the carbon spheres. The high chemical activity of the carbon spheres can have important applications in catalysis. The accretion of the carbon spheres may significantly improve the strength of composite materials made using the spheres.

The bonding in diamond is dominated by the sp³ electronic configuration, the four valence electrons of a carbon atom are all in the three-dimensional tetrahedral oriented sp³ hybrid orbital, forming strong σ bonding with the adjacent atoms. For graphite, the 3-fold coordinated sp² electronic configuration makes the three out of four valence electrons in a two-dimensional trigonally oriented sp² hybrid orbital, forming strong intralayer σ bonding within the hexagonal carbon rings; the fourth electron is in the π orbital which is perpendicular to the hexagonal network, forming a weakly unsaturated π bonding with adjacent layers. The discovery of C₆₀ has made a great impact on the understanding of carbon bonding. For a C₆₀, 12 pentagonal carbon rings must be introduced to form a close cage structure with 20 hexagonal carbon rings. Each atom in C₆₀ has three adjacent neighbors although the atoms may form pentagonal carbon rings. Thus, the nearest-neighbor distribution in C₆₀ is approximately equivalent to the atom distribution in a hexagonal graphite layer, and the electronic configuration can still be described by the sp² hybrid orbital although some distortion may exist due to the atom distribution in the C₆₀ cage. The fourth unsaturated π-bonding electron would like to form a pair with an electron from another C₆₀, forming the weakly bonded C₆₀ crystals. Thus, C₆₀ can function as an “element” that can be combined with other metallic elements, which can donate electrons, to form crystalline structure. Moreover, the C₆₀ cage is unlikely to be opened by an external electron due to the weakness of the unsaturated π bonding normal to the surface. Therefore, C₆₀ is considered to be chemically inert.

Carbon spheres with closed shell structure are expected to have analogous chemical characteristics as C₆₀. However, the situation could be very different if the graphitic layers composing the carbon spheres are unclosed, leaving many dangling bonds at the open sites. The study of chemical activity of carbon spheres, to our knowledge, has not been reported because of the lack of techniques for synthesized nanosize carbon spheres. Recently, we introduced a mixed-valence oxides catalytic carbonization (MVOCC) process for synthesizing monodisperse carbon spheres (or tubes) in macroscopic quantities at low cost and with high-purity product. The spheres are composed of graphitic flakes and are believed to exhibit many dangling bonds at the surfaces. In this paper, the accretion of the newly synthesized carbon spheres is demonstrated to show their high chemical activity. The accretion mechanism is discussed using a surface adsorption model.

To show the high chemical activity, the morphological and structural evaluations of the spheres are determined before and after being treated ultrasonically for 10 min in acetone. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the accretion among the spheres. Figure 1, parts a and b, show two SEM images of the carbon spheres before and after the treatment. The SEM images were recorded at 15 kV using a Hitachi S800.

Figure 1. SEM images of the carbon spheres (a) before and (b) after being treated in acetone for 10 min, showing the accretion of the spheres after the treatment. The SEM images were recorded at 15 kV using a Hitachi S800.

Figure 2. TEM images showing the (a) double and (b) triple accretion of the carbon spheres.

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of the curling graphitic flakes must have dangling bonds with unpaired sp$^2$ orbital. These sites are expected to be chemically active.

Various accretion geometry can be produced by a treatment in acetone. Figure 2 shows the double and triple accreted carbon spheres. The two spheres in Figure 2a are just attached on each other, and the three spheres in Figure 2b are tightly accreted. The intersphere is filled with “glue” type of material that has been identified as carbon using energy-dispersive X-ray spectroscopy. Figure 3 gives high-resolution TEM images of the accreted interfacial region of the two spheres shown in Figure 2a, and the corresponding regions are marked with A and B. The accreted region shows clearly the graphitic layered structure with interlayer distance approximately 0.34 nm, corresponding to the (002) interplanar distance of graphite. The interface of the two spheres can be seen in the region indicated by arrowheads in Figure 3b,c. The graphitic flakes can be as small as 1 nm. Some broken graphitic layers are visible at region B in Figure 3c, where the two spheres are separated by a thin amorphous layer.

To understand the mechanism for the formation of the accreted structure, we first review the structural model of these spheres as reported in detail elsewhere. Figure 4 shows a high-resolution TEM image of a carbon sphere before treated in acetone, showing unclosed graphitic flakes at the surface. The fine details seen at the surface are possible high-density chemical reaction sites, as indicated by arrowheads.
Make all the structural models observed experimentally. The lattice to be curved outward (with curvature. The heptagonal carbon ring forces the hexagonal network to curve inward. Therefore, the spheres are composed of curling graphitic flakes. Analogous chemical processes can occur if the edges of the graphitic flakes have pentagonal and/or heptagonal carbon rings. In general, no accretion by acetone is expected if the carbon spheres are composed of closed graphitic shells.

The rate of carbon sphere accretion in acetone is much faster than that in ethanol. This is probably because the ethanol molecule has much weaker electrostatic polarity than that of acetone, and it may not be strongly attracted by the graphitic flakes of the carbon sphere.

In conclusion, high chemical activity of the newly synthesized carbon spheres has been demonstrated. The accretion of the spheres is believed to be directly related to the hydrogen and/or oxygen atoms adsorbed at the edges of the open graphitic flakes. The high surface chemical reactivity of the carbon spheres clearly indicates that these spheres can be used as a support of catalyst. The accretion property of the carbon spheres may have important application to improve the strength of composite materials made using the spheres.

References and Notes

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