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Single titanium crystals encapsulated in carbon nanocages obtained by laser vaporization of sponge titanium in benzene vapor

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A technique, laser vaporization by ablating at a solid target in the vapor phase, is developed to produce encapsulated titanium nanocrystals. By vaporizing sponge titanium in benzene vapor, the single titanium crystals encapsulated in carbon nanocages have been synthesized in good yields. The sizes of the encapsulated crystals are around 5–15 nm and the numbers of the wrapped graphitic layers are on the order of 3–10 layers. Characteristic lattice spacings and angles observed by high-resolution transmission electron microscopy identify two phases of the nanocrystals inside the carbon onion cavities as α-Ti and β-Ti. The latter has never been stable below 850 °C until the experiment. The encapsulated titanium crystals adsorbed a large amount of hydrogen released in the synthesis. © *2000 American Institute of Physics.* [S0003-6951(00)03426-4]

Since the pioneering work of Ruoff *et al.*,[1] various nanocapsulates have been synthesized by using the arc-discharge method.[2] However, not all materials introduced into the arc plasma could be encapsulated into carbon cages and most of them are in the form of their carbides.[3] The iron-group metals, Fe, Co, and Ni, are the only elements which can be encapsulated in the form of metal particles.[4] Various efforts have been focused on encapsulating other metal nanocrystals, especially Ti,[5] into the carbon cages, but no further success has been reported so far. For instance, Seraphin and Jiao have co-deposited 20 elements with carbon in an arc discharge, but the encapsulated metal particles are still restricted to Fe, Co, and Ni.[6] The restriction has been attributed to the arc-discharge reaction.

The laser vaporization technique seems to be more effective in preparing such material. When sponge titanium was selected as the solid target and benzene vapor as the environment of laser vaporization, carbon-encapsulated metallic titanium nanoparticles were created.

In the experiment, the vaporization laser is the fundamental output of a Q-switched Nd:YAG laser. The laser beam was focused on the target with a power density near 10^9 W/cm^2. The titanium target was located just above the liquid benzene surface. The target and the liquid were sealed in a glass container at room temperature. Before the experiment, the container was bubbled with argon to keep the system out of air.

After 3 h of laser vaporization, the container was covered with a fine black powder, which weighed about 400 mg, while the benzene was still almost colorless, suggesting that very few products can be dissolved in benzene. Replacing benzene with toluene gave a similar result, but other organic solvents, such as hexane and cyclohexane, produced very few products in the same condition. In addition to sponge titanium, foils of other transition metals, such as iron, nickel, and titanium, were also selected as the targets of laser vaporization. The black powder could also be produced from the targets, but with much lower yields.

The composition of the black powder was analyzed by atomic spectroscopy and elemental analysis. According to the chemical analysis, the products are composed of 84.05% C and 2.26% H in weight. Inductively coupled plasma-Atomic-emission spectroscopy analysis measured titanium content of 10% by weight.

Transmission electron microscopy (TEM) of the powder was performed on a JEOL 2010EX microscope operated at 200 kV. Figure 1 is a TEM image of the powders, which are shown as uniform balls in size about 10–15 nm. The high-resolution TEM image of isolated nanoparticles is displayed in Fig. 2(a). The particles are shown to consist of multilayered concentric graphitic shells encapsulating a single crystal, as evidenced by the regular set of lattice fringes. The size distribution of the particles was measured by the Brunauer–

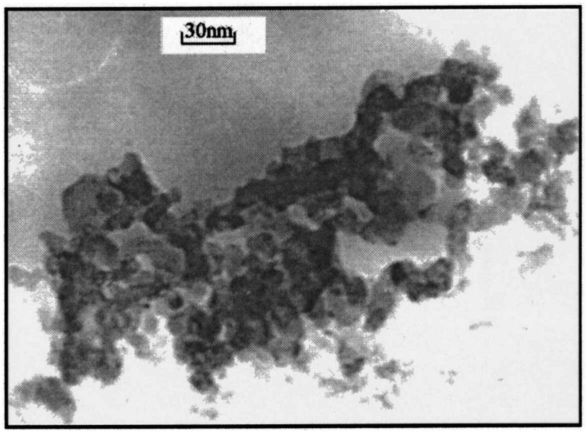

FIG. 1. TEM image of the nanoparticles produced by laser ablating sponge titanium in benzene vapor. The particles are shown to have uniform sizes (10–15 nm) and uniform ball shapes.

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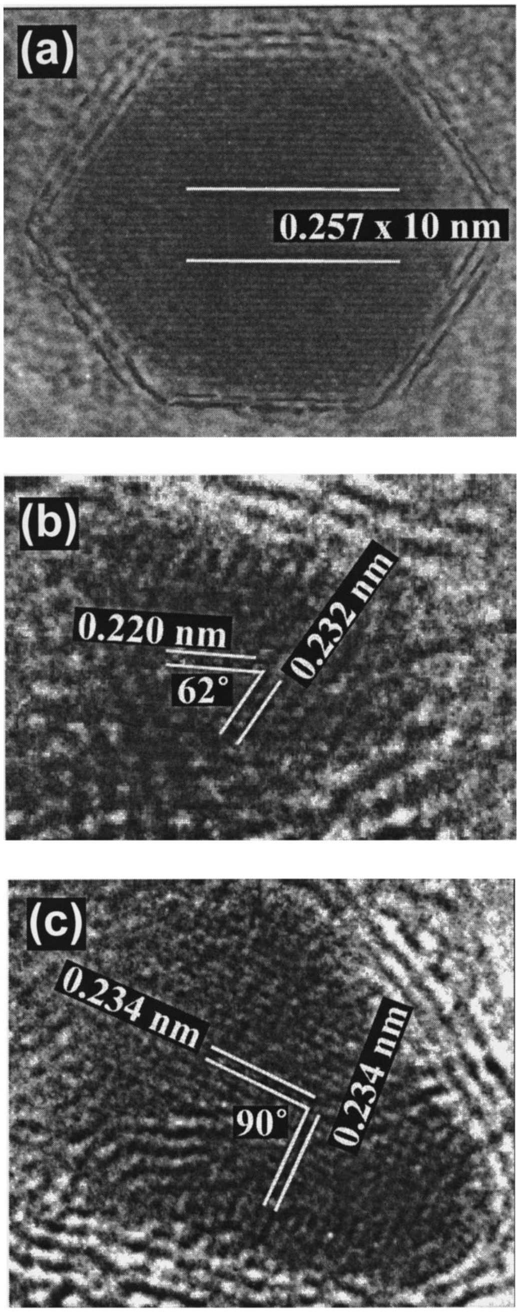

FIG. 2. High-resolution TEM images of the particles. They are shown to be multilayered graphitic cages encapsulating nanocrystals. Images of the nanocrystal showing different planes or phases are amplified in (a), (b), and (c).

Emmett–Teller method. According to the measured surface areas and pore volumes, the sizes of most of the products are on the order of 10–15 nm. In fact, the diameters of almost all the particles observed in the TEM images fall in this range.

By examining the fringes of the encapsulated crystals, three different fringe patterns can be distinguished. Their TEM images are shown in Figs. 2(a), 2(b), and 2(c). From the experimental condition and the result of the composition analysis, the encapsulated crystals can only be Ti, TiC, or TiO_2, which can be identified by the known characteristic lattice (d) spacings of the species. In the crystal shown in Fig. 2(c), two perpendicular planes with equal spacing of 0.234 nm are observed. The observed spacings agree well with those of the (101) plane ($d = 0.2338\,\text{nm}$) and (110) plane ($d = 0.2338\,\text{nm}$) of β-Ti,[7] which has a body-centered-cubic structure.

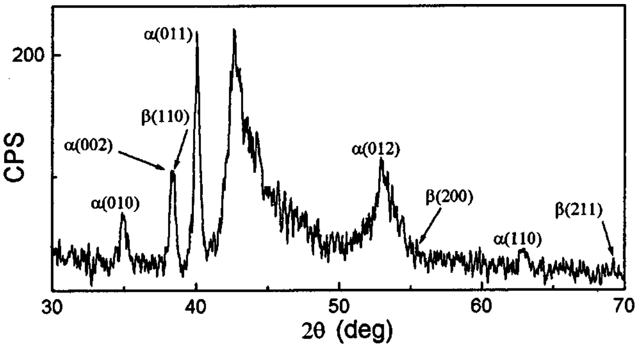

FIG. 3. X-ray diffractogram of the particles. $\alpha(hkl)$ and $\beta(hkl)$ denote the α-Ti (hkl) and β-Ti (hkl) peaks in the graph, respectively. The broad peak is contributed from the carbon cages showing mainly amorphous carbon.

Figures 2(a) and 2(b) display the other phase of the nanocrystals encapsulated in the carbon cages. Both crystals are α-Ti with a hexagonal lattice structure, but showing different crystal planes. Observed in Fig. 2(a) are (010) planes of α-Ti with the distinct d spacing of 0.257 nm, which matches quite well with the literature value, 0.2557.[7] Two characteristic d spacings of (011) and (002) planes of α-Ti crystal were observed in Fig. 2(b), with the literature values[7] in parentheses: 0.220 nm (0.2244) and 0.232 (0.2342). The crossed angle of the planes, 62°, also matches the literature value (61.4°).[7]

In addition to the crystals shown in Fig. 2, other encapsulated crystals with quality fringe patterns were also surveyed, and α-Ti and β-Ti are the only phases observed in the TEM measurement. The presence of phases of both α-Ti and β-Ti are confirmed in the x-ray diffractogram (Fig. 3) of the products, while the former is apparently in a larger amount.

The β-Ti phase can only be formed and stabilized above 850 °C.[8] Vaporization of the pulsed laser beam can reach the temperature, but the phase of the crystals were preserved and observed in room temperature. The preservation may be related to the encapsulation of the carbon cages. During the past five years, some approaches have been taken in an attempt to encapsulate titanium metal by arc discharge without success. The failures of producing caged titanium particles have been attributed to the strong tendency of forming titanium carbide compounds.[6] As a matter of fact, while various encapsulated nanoparticles have been produced by the means of arc discharge, most of the encapsulated materials are metal carbides.[9] The selection was found to be determined by some physical properties of the material.[6] The laser ablation technique, however, seems not to be affected by the criteria. Although the experiment involves solid, liquid, and gas phases, its device and conditions are not very complicated: No vacuum or high pressure; no heating or cooling. The technique is easy to use and can certainly be applied to synthesize carbon nanocages filled with different materials.

During the experiment, the products in the gas phase were also collected and analyzed by gas chromatography-mass spectroscopy (GC-MS), which detected hydrogen and various hydrocarbons such as methane and acetylene. From the characterization of the products, it can be suggested that, in the experiment, the benzene vapors were adsorbed onto

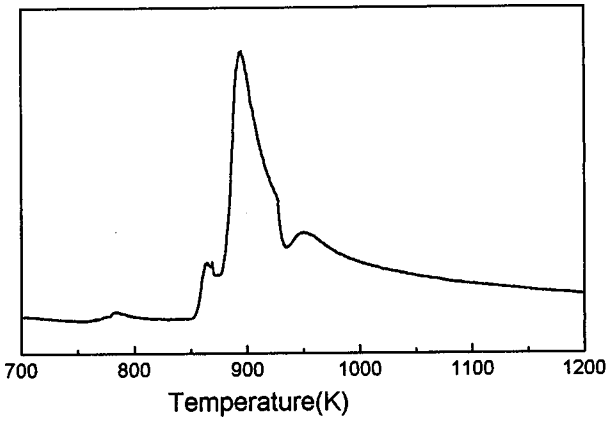

FIG. 4. Hydrogen release curve of the product obtained as a function of the heating temperature.

the sponge titanium surface that has a large surface area due to its porous structure. The adsorbed benzene molecules were partly carbonated by the vaporizing laser, forming nanoparticles consisting of several nested layers. Meanwhile, titanium particles were also ablated by the laser beam. They condensed as nanocrystals and were enclosed into the cavities of the carbon onions.

While the benzene molecules were carbonated by the photodissociation, a vast amount of hydrogen was released and adsorbed on the surface of the titanium nanograins. The hydrogen was not only measured by the elemental analysis, but it was also detected by the GC-MS analysis when the particles were heated. Figure 4 shows the hydrogen release curve which plots the amount of desorbed hydrogen versus the heating temperature.

Titanium is one of the best hydrogen adsorbing elements known, especially when in the size of nanometers. The large surface-to-volume ratio tied to such small diameters would bring up rapid oxidation of the titanium nanograins, but the problem is solved by the chemical resistance of the graphite cage. If multilayered shells of the carbon cage can be reduced to a single wall, the shell might be an ideal film which prevents the encapsulated titanium particle from oxidation but allows the hydrogen molecules to pass through. We are optimizing the experimental conditions in order to produce a hydrogen-storage material.

The laser vaporization technique was developed in this laboratory and has been applied for the encapsulation experiment. The experiment involves three phases, but the device is rather simple and the experiment was operated at room temperature and in normal pressure. The laser vaporization synthesis has good yield: Over 100 mg of products can be produced in each hour. The sizes and the shapes of the nanoparticles are quite uniform. It is possible to optimize the experimental conditions to produce single-walled encapsulated nanoparticles. The technique can be applied to synthesize different encapsulated nanocrystals and other material. Experiments are in progress.

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