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PAPER

Luminescent hollow carbon shells and fullerene-like carbon spheres produced by laser ablation with toluene

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Hollow carbon shells and fullerene-like carbon spheres are prepared by laser ablation with toluene molecules as a carbon precursor. The liquid carbon precursor is superior to the gaseous carbon precursors conventionally used, such as C_2H_2, due to its safety and ease of handling. The formation mechanism of these carbon nanostructures is discussed. The laser irradiation-induced high temperature results in the decomposition of toluene molecules to carbon atoms. Consequently, these carbon atoms nucleate and grow to novel carbon nanostructures as the temperature drops. The graphene-like hollow carbon shells show strong and excitation wavelength-dependent light emission, which has potential optical applications.

Introduction

Carbon nanostructures involving nanotubes, fullerenes and graphenes have received considerable attention due to their unique and novel properties, such as corrosion resistance, tailorable pore structure and good electronic conductivity,[1–5] all of which allow them to be used in catalysis,[6,7] optical devices[8] and hydrogen storage,[9,10] to name but a few. The strong and tunable luminescence of carbon nanostructures, together with their biocompatibility, further extend their applications to bio-related areas (*e.g.*, biological labeling).[11–16] As is well-known, the crystalline status of carbon structures will inevitably affect their properties with respect to electronic conductivity and catalysis. It is commonly accepted that well-crystallized carbon nanostructures are difficult to fabricate through conventional synthesis methods due to the ultrahigh crystalline temperature of carbon species (>1500 °C).[1,17]

Laser ablation in liquids is well known to produce non-equilibrium conditions, with local high temperatures (several thousands Kelvin) and high pressures (about 1 GPa).[18–26] During irradiation of liquid toluene with a high power laser beam, hollow carbon shells (graphene-like) and fullerene-like carbon spheres can be successfully prepared. The formation mechanism of these hollow carbon shells and fullerene-like carbon spheres has been discussed. Initially, the laser irradiation-induced high temperature results in the decomposition of toluene molecules into carbon atoms. These carbon atoms will form hollow carbon shells as the temperature decreases. Consequently, these hollow carbon shells will aggregate to form larger-sized web-like carbon coagulations. When these carbon aggregates suffer from secondary laser irradiation, their temperature will increase to several thousand Kelvin, which is high enough to evaporate a significant amount of the carbon atoms. These evaporated carbon atoms will nucleate at the interface between the bubbles formed by laser ablation and the surrounding liquid toluene medium, resulting in the formation of fullerene-like carbon spheres. This study deepens our understanding of the formation mechanism of novel nanostructures through the laser ablation of organic reagents. A strong blue light emission and excitation wavelength-dependent photoluminescence (PL) of the hollow carbon shells is observed. These fluorescent hollow carbon shells may have optical applications, as well as applications in the catalysis and drug delivery communities[27] due to their hollow structure.

Experimental section

A piece of cleaned silicon wafer was fixed as a target and immersed in pure toluene (about 8 ml). A Nd:YAG laser operated at 1064 nm with a pulse duration of 10 ns and a frequency of 10 Hz was used to irradiate the target. The fluence of the laser ranged from 70 to 150 mj pulse^{-1}. The liquid was continuously stirred during the laser ablation process. The laser beam was focused on the Si target with a spot size of about 2 mm in diameter using a lens with a focal length of 150 mm. After irradiation for about 1 h, the transparent toluene liquid became opaque and many black aggregates were suspended in the liquid. Further irradiation for about 2 h gave rise to the formation of fullerene-like carbon spheres. These black aggregates were collected by centrifugation at 4000 rpm for 20 min. Low speed centrifugation could separate the large-sized carbon species from the small amount of small-sized SiC nanoparticles (size < 5 nm)

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formed at the initial stage of the laser ablation process. Their morphology was observed by scanning electron microscopy (SEM) (Sirion 200 FEG). A microstructural examination was conducted on a transmission electron microscope (TEM, JEM-200CX) with a 200 kV acceleration voltage by dropping a drop of the liquid onto a carbon-coated Cu grid. PL measurements of the carbon aggregates dispersed in ethanol were recorded on a FLS920 PL spectrophotometer with an Xe lamp at room temperature.

Results and discussion

Fig. 1a shows the SEM image of the product after the laser irradiation of toluene for 2 h, demonstrating many spheres with a mean diameter of about 600 nm. There are several cracks on each sphere (see circle marks in Fig. 1a), which might be formed during the SEM measurements under the vacuum conditions. Further TEM results indicate that these spheres are not solid (or partially hollow), as shown in Fig. 1b. The nanoshells are composed of perfectly crystallized graphite (002) planes, as shown in the inset of Fig. 1b. The nanoshells can be deemed to be 21 graphite (002) planes stacked together, similar to a fullerene structure, as shown in Fig. 1c. The selected area electron diffraction (SAED) pattern further verifies the presence of well-crystallized carbon structures with a plane distance of 0.34 nm, in agreement with the value of the graphite (002) plane (Fig. 1d, circle mark). Therefore, through laser ablation of pure liquid toluene, fullerene-like carbon spheres with ultrathin and perfectly crystallized nanoshells can be prepared.

Further investigations reveal that the laser fluence is effective in controlling the diameter of the fullerene-like carbon spheres. Fig. 2a shows a TEM image of the sample prepared with a 70 mj pulse^{-1} laser fluence. The corresponding size distribution of these hollow spheres is shown in Fig. 2b by randomly counting more than 100 spheres. The mean size is about 700 nm, with a wide size distribution ranging from 550 to 850 nm. When the laser fluence is increased to 150 mj pulse^{-1}, the mean size of the hollow spheres

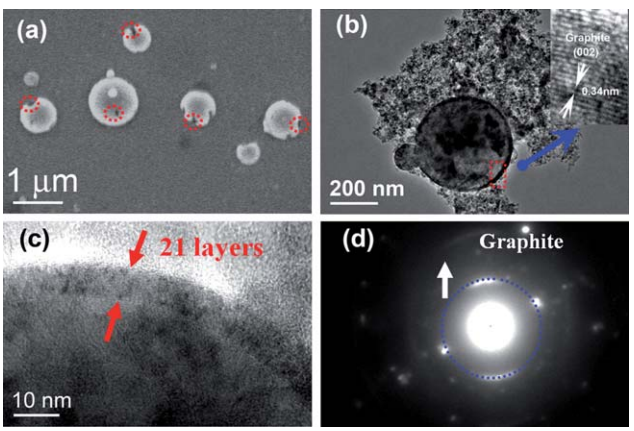

Fig. 1 The morphology and microstructure of the fullerene-like carbon spheres obtained by the laser ablation of toluene for 2 h. The laser fluence was 100 mj pulse^{-1}. (a) SEM image; circle marks show a few cracks. (b) TEM result; inset: high resolution TEM image. (c) High resolution TEM image of the shell structure. (d) SAED pattern; the circle mark corresponds to the diffraction of the graphite (002) plane.

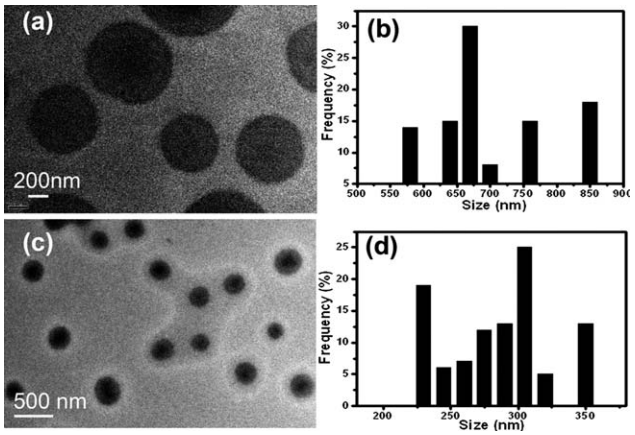

Fig. 2 TEM images of the fullerene-like carbon spheres prepared under different laser fluences. (a) and (c) are related to 70 mj pulse^{-1} and 150 mj pulse^{-1}, respectively. (b) and (d) show the corresponding size distributions of the fullerene-like carbon spheres.

reduces to about 300 nm (Fig. 2c and 2d). The size reduction as the laser fluence increases is the same as the size evolution of Si nanoparticles prepared by laser ablation.[28] To date, there are few reports on the formation of spheres with such a large size (>500 nm) by laser ablation in a liquid.[26] Hence, it is important to explore the formation mechanism of these fullerene-like carbon spheres, which will direct the future synthesis of novel nanostructures (*e.g.*, hollow spheres and nanorings) based on the laser ablation in a liquid approach.

In order to explore the growth mechanism of these fullerene-like carbon spheres, the products prepared by laser ablation at different times were studied. After laser ablation for 45 min, a few black aggregates were obtained. TEM observations showed that these black aggregates were web-like (Fig. 3a). The enlarged image demonstrates that many voids exist within the web-like aggregates (Fig. 3b, arrow marks). Hollow carbon shells are observable in the further-magnified image (Fig. 3c). The shells are formed with several layers (< 5) of graphite (002) planes. The SAED pattern further confirms the crystalline structure of the hollow carbon shells (inset in Fig. 3c). The Raman spectrum (Fig. 4) also demonstrates the presence of sp^2-bonded carbon phases with a characteristic disorder (D peak), and graphitic (G peak) bands at 1347 and 1574 cm^{-1}, respectively.[8,29] 2D, 2G and combination bands (D + G) are also observable in the Raman spectrum, which are consistent with the Raman spectrum of graphene with defects.[30] Therefore, the hollow carbon shells have a graphene-like structure. As the laser ablation process proceeds (after about 1 h), big spheres emerge with partially crystallized shells (Fig. 3d). When the ablation time reaches 2 h, fullerene-like carbon spheres are obtained (Fig. 1 and Fig. 2).

Based on the above experimental results, the formation mechanism of the carbon nanostructures can be understood. When the high power laser beam irradiates the silicon target, the energy is absorbed by the Si target and leads to the formation of an Si plasma with a local high temperature (about 6000 K) and high pressure (about 10 GPa) at the interface of the Si target and the surrounding liquid toluene medium.[18–26] Subsequently, the Si plasma will ultrasonically and adiabatically expand, resulting in cooling of the Si plume region, and hence to the formation of

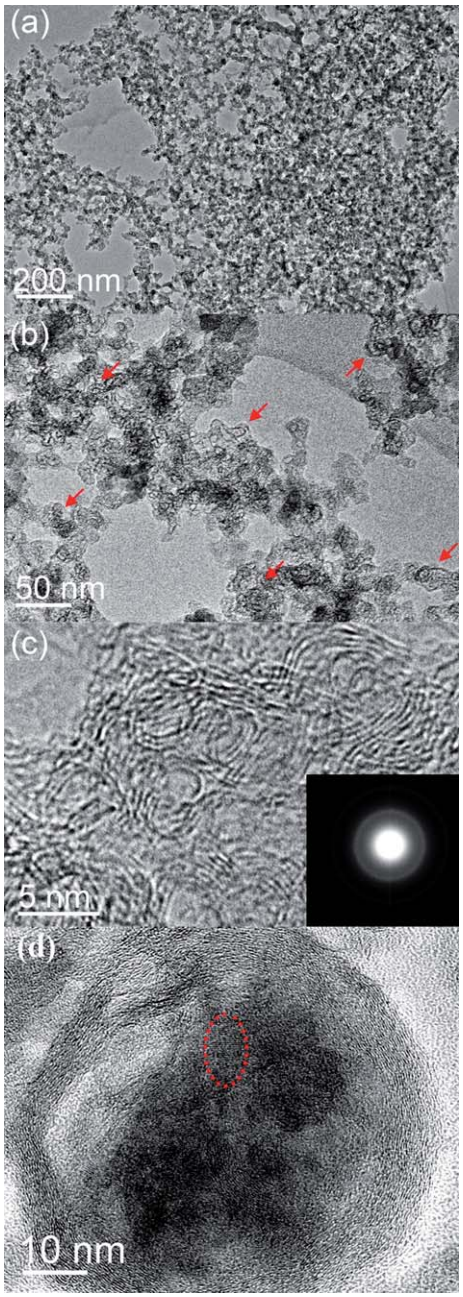

Fig. 3 TEM images of the carbon nanostructures obtained by laser ablation at different times. (a) to (c) are acquired at 45 min. (a) Low magnification image of the web-like carbon aggregates. (b) Magnified image showing that many voids (see arrow marks) are involved in the aggregates. (c) High resolution TEM image of the hollow carbon shells. The shell is composed of less than 5 layers of graphite (002) planes; inset: SAED pattern. (d) TEM image of the carbon spheres prepared after laser ablation for 1 h. The red circle marks an SiC nanoparticle.

Si clusters. Meanwhile, the decomposition of toluene molecules occurs near to the hot Si plasma region according to eqn (1), as shown in Fig. 5a. This process is verified by the fact that a few bubbles (mainly hydrogen) ascend from the Si target and float on the liquid surface during the laser irradiation process.

$$CH_3C_6H_5 \rightarrow 7C\ (\text{atoms}) + 4H_2\uparrow \quad (1)$$

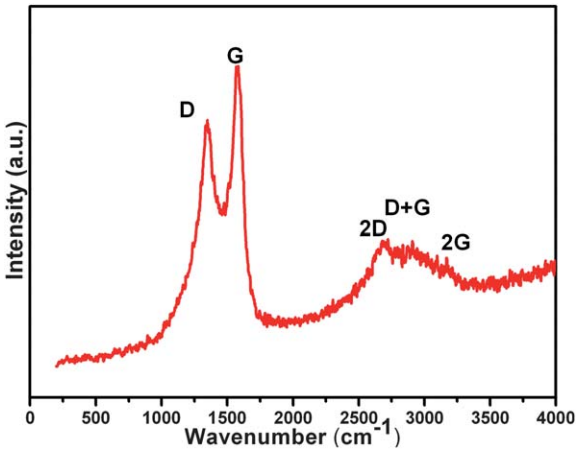

Fig. 4 Raman spectrum of the hollow carbon shells.

Some of the carbon atoms decomposed from toluene molecules will react with the hot and active Si clusters, giving rise to the formation of silicon carbide quantum dots (see circle marks in Fig. 3d), which has been reported before.[23] A large amount of the residual decomposed carbon atoms will coagulate to form hollow carbon shells (Fig. 3c). Subsequently, these hollow carbon shells will aggregate together to induce large-sized web-like carbon coagulations with a black colour (Fig. 5b and Fig. 3a). These carbon aggregates have the opportunity to suffer from the secondary laser beam. In turn, the energy of the high power laser beam is absorbed by these carbon aggregates. The local temperature of the aggregates will be instantly increased to several thousand Kelvin (much higher than the temperature

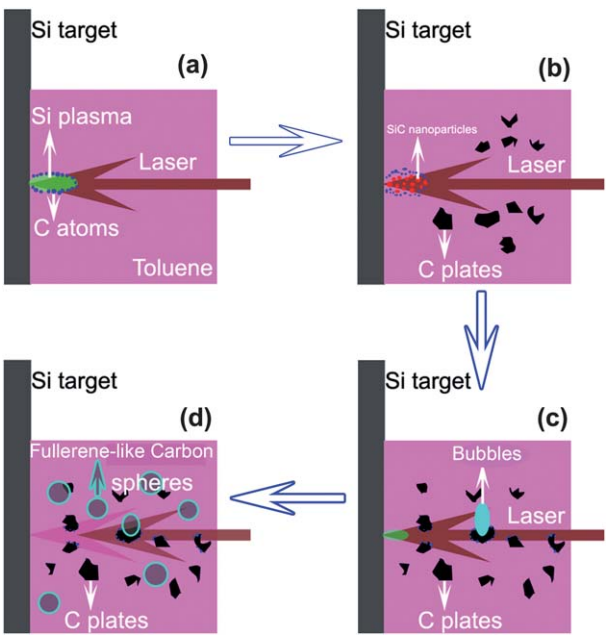

Fig. 5 Schematic illustration of the proposed formation process of these fullerene-like carbon spheres. "C plates" stands for the aggregates of hollow carbon shells. The size of the "laser beam", "Si plasma", "C plates" and "Fullerene-like carbon spheres" depicted is not in proportion.

available by conventional fabrication methods),[31,32] which is high enough to evaporate a substantial proportion of the carbon atoms (Fig. 5c). These evaporated carbon atoms will nucleate and grow at the interface between the bubbles (induced by laser heating of toluene and/or decomposition of toluene molecules to hydrogen gas) and the surrounding liquid toluene medium, resulting in the formation of fullerene-like carbon spheres (Fig. 5d). The supposed formation mechanism of these carbon nanostructures during laser ablation is sustained by the following fact. At the start, the laser beam is able to penetrate the transparent toluene liquid and reach the surface of the Si target, emitting a crepitating sound following each laser shot. However, when the irradiation process lasts for about 45 min, a clear light beam can be observed with the naked eye. This is ascribed to the formation of large-sized web-like carbon aggregates. These aggregates will scatter and absorb most of the laser energy, preventing it from reaching the Si wafer surface. After about 55 min of laser ablation, much black agglomerate is suspended in the brown liquid. This severely screens the laser beam, and the laser beam will attenuate entirely in the liquid, together with the disappearance of the crepitating sound. This process was recorded by a camera, as shown in Fig. 6, showing the moment when a laser shot irradiates the toluene liquid. We can see a bright laser beam in the liquid that attenuates gradually during propagation. On the top surface of the liquid, there are some black coagulations, which should be carbon aggregates based on the above discussion.

Strong blue PL from the hollow carbon shells was observed under an excitation wavelength of 340 nm (curve d in Fig. 7). The PL peak exhibits a prominent excitation wavelength-dependence. The full width at half maximum (FWHM) of the PL peak decreases as the excitation wavelength shifts to longer wavelengths. According to quantum confinement effect theory, the band gap of the nanostructures increases with the reduction of the size of the nanostructures. Here, the hollow carbon shells have a broad size distribution. Therefore, as the excitation light moves in the blue direction, small-sized hollow carbon shells (with larger band gaps) can be excited and contribute to the light emission. This will cause the emission peak to shift towards the short wavelength direction, which is in agreement with the trend shown Fig. 7. Simultaneously, the amount of hollow carbon shells that contribute to the emission increases, resulting in the enlarged FWHM of the emission spectrum (Fig. 7). Furthermore, the thickness of the hollow carbon shells is less than 2 nm

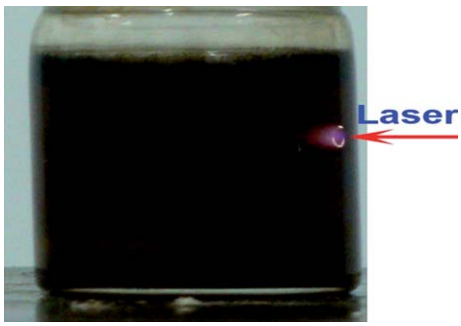

Fig. 6 A snapshot of a single laser shot irradiating the toluene liquid, taken after laser ablation for 45 min. A laser beam can be clearly seen in the toluene liquid.

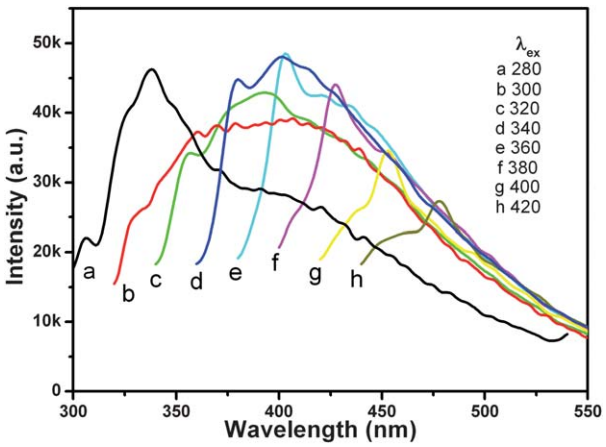

Fig. 7 PL spectra of the hollow carbon shells under different excitation wavelengths. Curves a to h are related to excitation wavelengths from 280 to 420 nm with 20 nm steps between each curve.

(Fig. 3c). Taken together, the strong PL emission is temporarily ascribed to the quantum confinement effect.[12] Also, according to previous calculations, the energy gap in the visible spectral range can be obtained from graphene fragments with a diameter of about 2 nm,[33] which is in accordance with the value of the hollow carbon shells prepared here.

Conclusions

In summary, hollow carbon shells and fullerene-like carbon spheres were fabricated by the laser ablation of liquid toluene. The laser irradiation-induced high temperature results in the decomposition of the toluene molecules to carbon atoms. These carbon atoms further nucleate and grow into novel carbon nanostructures. Here, toluene is used as a carbon precursor to synthesize carbon nanostructures, which is superior to other gaseous precursors, such as the explosive and highly toxic C_2H_2. Detailed studies of the formation mechanism of these carbon nanostructures is of prime importance to direct the fabrication of other novel nanostructures using the laser ablation in liquids protocol. The hollow carbon shells can emit strong blue light due to the quantum confinement effect, which gives them potential applications in optical and biological areas, such as biological labeling.

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