

PURIFICATION AND CHEMICAL MODIFICATION OF ONION-LIKE FULLERENES

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Abstract

As carbon allotrope, onion-like fullerenes (OLFs) have been limited in applications due to their strong hydrophobicity. In this paper, OLFs were modified by three methods including toluene reflux, melted salt reaction and in situ-oxidation in radio frequency plasma atmosphere. The raw OLFs prepared by chemical vapor deposition (CVD) were purified by HNO₃ treatment, and then modified on surface by reflux with K in toluene and reaction with melted KOH. On the other hand, in order to conduct in-situ modification on OLFs, oxygen was introduced into radio frequency plasma atmosphere after Huainan coal and ferrocene were reacted in Ar plasma for an hour. The raw, purified and modified products were characterized by high resolution transmission electron microscopy (HRTEM), thermogravimetric analysis (TGA) and Fourier transform infrared (FT-IR) spectroscopy. Results proved the formation of OLFs (OH)_n. The formation mechanisms of OLFs(OH)_n were also discussed.

Introduction

As a new member of fullerenes family, Onion-like Fullerenes (OLFs) have attracted intensive attentions and become the focus of studies in advanced material field since reported in 1992. The particular properties and applications of OLFs are determined by their special cage structures. Many efforts have been made to create these onions and several techniques have been developed to synthesize them, such as arc discharge, electron irradiation, chemical vapor deposition (CVD) and plasma-enhanced CVD methods. However, their applications in many fields, such as photoelectricity, bio-medicine and chemical industry, have been influenced due to their strong hydrophobicity. Up to date, most studies on modification of CNTs and C₆₀ have been focused. In contrast, few reports can be found about purification and modification of OLFs. In this paper, the raw OLFs were modified by three methods including toluene reflux, melted salt reaction and in-situ oxidation in radio frequency plasma atmosphere. The formation mechanisms of OLFs(OH)_n were also discussed. All of these cast a basis for the study of the properties and applications of OLFs.

Experimental

Purification of OLFs

The raw OLFs, which were obtained by CVD with C₂H₂ as carbon resource and ferrocene as catalyst precursor, was heated and refluxed in HNO₃ of 2.6 mol·L⁻¹ at 100 ° for 24 h. After oxidation was completed, the supernatant phase was separated and filtered by microporous filtering film and membrane filter after being cooled to room temperature. The resulted samples were then repeatedly washed to neutral pH using deionized water in order to remove any excess oxidizing agent and water soluble compounds. Subsequently the samples were dried in a drying oven at 100 ° for 24 h. Here the material obtained in this step was referred as purified OLFs.

Modification of OLFs by reflux with K in toluene

In this process, 100 mg of the purified OLFs were sonicated in 100 ml of toluene. The mixture was refluxed at 100 ° for 2.5 h in an Ar gas atmosphere while 10 mg of K was added to toluene solution. Deionized water was added to residual deposit after the toluene solution was filtered. The supernatant phase was then collected and dried in a drying oven at 100 °. Here the material obtained in this step was referred as modified OLFs by toluene.

Modification of OLFs by reaction with melted KOH

In this process, 100 mg of the purified OLFs were melted with 200 mg of solid KOH for 5 min. After the system reached room temperature, 10 ml of deionized water was added into the reactor. The resulted solution was then poured into 100 ml of methanol; the black solid was then extracted by centrifuge. This procedure was repeated thrice and the solid material was dried in a vacuum drying oven for at least 24 h.

Modification of OLFs by in-situ oxidation in radio frequency plasma atmosphere

In this work, Huainan washing coal and ferrocene were used. The as-obtained coal sample was crushed and sieved to 100 meshes, and dried at 383 K for 12 h before use. The mixture of 0.30 g coal and 0.03 g ferrocene was used directly as reactants. The device used in this work was SY type 500W radio frequency plasma reactor. The plasma was excited by the high-frequency coil around the chamber made of quartz tube. After the reactant was put into radio frequency chamber, Ar gas was flowed at the rate of 22.0 ml·min⁻¹ and the pressure was kept constant at 30 Pa, the radio frequency output was kept at 400W. O₂ with a flow rate of 1.2 ml·min⁻¹ was introduced into system for 30 min after reaction were hold for 1 h, then the sample was cooled to room temperature under argon atmosphere. The matter deposited on the inner wall of the chamber was collected.

Characterization of the samples

High resolution transmission electron microscopy (HRTEM) and Fourier transform infrared (FT-IR) spectroscopy were employed to characterize the raw, purified and modified OLFs. HRTEM was performed on a JEM-2010 at 200 kV. FT-IR spectra were recorded on a PERKIN-ELMER 1730 spectrometer. Thermal behavior of the raw and purified samples was investigated by thermogravimetric analysis (TGA, Separam TGA-92). Samples were heated at 10 °·min⁻¹ up to 1000 ° in flowing air.

Results and discussion

Purification of OLFs

HRTEM images of all samples are shown in Figure 1. Figure 1(a)-(d) show images of the raw and purified OLFs by HNO₃ treatment. Figure 1(b) shows the zoom-in view of the rectangle labeled part in Figure 1(a). From Figure 1(a) and Figure 1(b), it can be clearly observed that the raw materials were mostly metal-encapsulating OLFs with few impurity such as carbon nanotubes (CNTs) and amorphous carbon. Figure 1(c) is HRTEM image of purified OLFs and Figure 1(d) is enlarged image of the rectangle labeled part in Figure 1(c). CNTs and OLFs were effectively separated, most amorphous carbon and metal particles were removed by nitric acid treatment, and majority OLFs were hollow, as shown in Figure 1(c) and Figure 1(d). It was suggested that metal particles and other carbon impurity were removed by HNO₃ oxidation, thus improving the purity of OLFs.

TG/DTG analysis in an air atmosphere was also performed on samples before and after purification for further determining the result of purification, as shown in Figure 2. TG curve of the raw OLFs shows one well defined weight loss between 413 and 619 °, as shown in Figure 2(a). There was nearly no weight loss below 313 °. A little weight increase between 313 and 413 ° was probably attributed to oxidation of Fe nanoparticles. A rapid weight loss began at 413 ° and ended at 619 °, corresponding to about 62.2 wt.% of total mass, which indicated a 26.5 wt.% of Fe content in the raw OLFs. DTG curve shows a peak at 484 °, indicating the maximum burning rate. The broadening of the DTG curve was due to the occurring of a small shoulder peak, implying the overlap of different combustion processes of

amorphous carbon, CNTs and OLFs.

TG/DTG curves of the purified OLFs are shown in Figure 2(b). The TG curve shows a slow weight loss at temperature between 200 and 480 °, followed by an abrupt weight loss up to 655 °. This indicates that the very small amount of amorphous carbon in purified OLFs was burnt out at temperature below 411 ° and the majority of OLFs was burnt over 480 °. The weight loss was about 89.7 wt.% of total mass at 655 °, which indicated a 7.2 wt.% of Fe content in purified OLFs. DTG curve shows one peak at 571 °, that is the maximum burning rate. It is worthy to note that this temperature for maximum burning rate was much higher than that for raw OLFs. High burning temperature indicates that amorphous carbon attached to OLFs was removed and most of metal particles were removed by HNO₃.

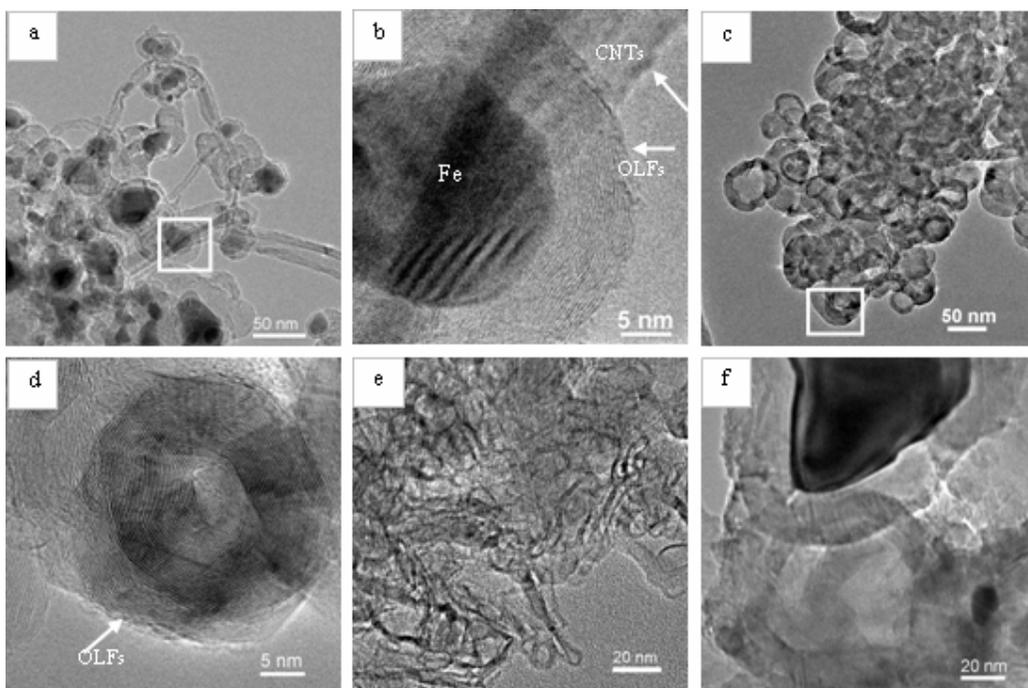


Figure 1. HRTEM images of raw OLFs (a, low magnification; b, high magnification), purified OLFs (c, low magnification; d, high magnification), modified OLFs (e) through reflux with K in toluene and (f) through reaction with melted KOH.

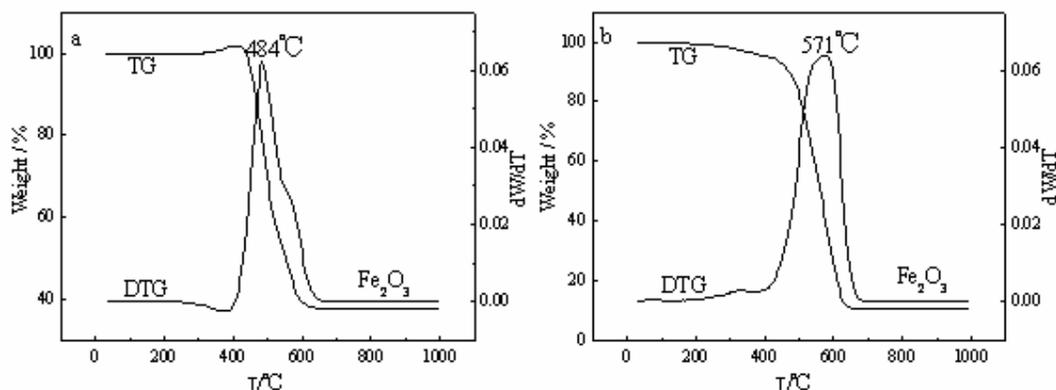


Figure 2. TG/DTG curves of raw OLFs (a) and purified OLFs (b)

Modification of OLFs by toluene reflux and melted KOH

Figure 1(e) shows HRTEM image of OLFs modified by reflux with K in toluene. The modified OLFs were overlapped each other. Their structures were altered comparing with purified OLFs, probably because of the asymmetric C=C bonds and very strong hydrogen bonds after a great deal of hydroxyl groups were attached to OLFs. Figure 1(f) shows HRTEM image of OLFs modified by reaction with melted KOH. The diameters of modified OLFs became larger than those of purified OLFs, similar to fullerols.

Figure.3 shows the FT-IR spectra of purified and modified OLFs. The bonds at 3468 cm^{-1} was ascribed to the vibration of the -OH groups, mainly in H_2O , as shown in Figure 3(a). The absorption peak of -C=C- groups in OLFs, with symmetric structures of cages, was rather weak due to double bonds locating in symmetric center of molecules. This confirms that no many new groups were introduced onto the surface of OLFs after HNO_3 treatment. In contrast to purified OLFs, there were many changes for modified OLFs by toluene reflux, as shown in Figure 3(b). The stronger peak at 3451 cm^{-1} , which is attributed to stretching vibration of -OH groups, suggested that there were more -OH groups in modified OLFs than those in purified OLFs. The obvious bonds at 1630 cm^{-1} and 1039 cm^{-1} were assigned to the absorption peaks of the C=C and C-O bonds, respectively, and the peak at 1402 cm^{-1} was ascribed to bending vibration of -OH bonds, further confirming formation of hydroxyl compound (denoted as $\text{OLF}(\text{OH})_n$). The FT-IR spectra of modified OLFs through reaction with melted KOH are shown in Figure 2(c). The strong peak at 1099 cm^{-1} , corresponding to stretching vibration of -OH groups, confirmed that -OH groups were attached to the surface of modified OLFs to form $\text{OLF}(\text{OH})_n$.

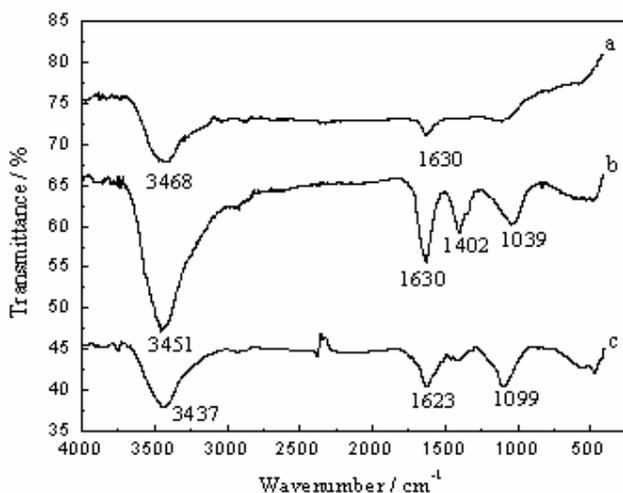


Figure 3. FT-IR spectra of purified (a) and modified OLFs (b) through reflux with K in toluene and modified OLFs (c) through reaction with melted KOH.

The study on water-soluble fullerol by reaction of C_{60} with K in toluene solution has been reported. Because the cage structures of OLFs are similar to those of C_{60} , $\text{OLF}(\text{OH})_n$ was synthesized by reaction of OLFs with K in toluene. The spherical products, with black deposit on their surfaces and insolubility in toluene and water, were produced during reaction. A lot of black deposits, which might be $\text{K}_n(\text{OLF})_n$ obtained by reaction of OLFs with K, were adhered on the inner wall of flask after reaction, similar to K_nC_{60} prepared by reaction of C_{60} with K. $\text{K}_n(\text{OLF})_n$ were quickly hydrolyzed to form $\text{OLF}(\text{OH})_n$ by the action of water molecules, as shown in Figure 4. FT-IR measurement confirmed that the C=C and C-O bonds existed in modified OLFs. C=C bonds were broken to create C-OH bonds in order that non-polar C=C bonds were transformed into polar C-OH bonds.

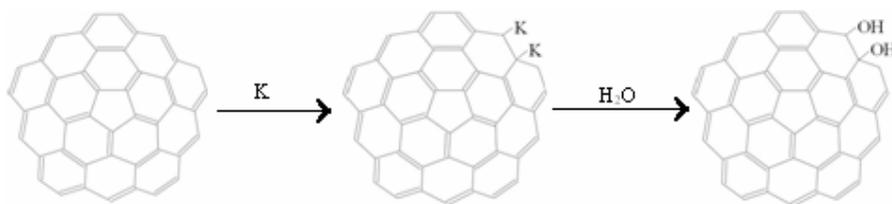


Figure 4. Possible mechanism of OLFs(OH)_n produced by reflux with K in toluene

As far as the surface modification of OLFs by KOH is concerned, hydroxyl groups could be viewed as outcome of addition and oxidation of electrophilic hydroxyl free radicals, which were obtained by reaction of OLFs with KOH, on the unsaturated C=C bonds on surface of OLFs. Hydroxyl free radicals have very strong ability of addition reaction because of their electron-defect nature, high electronegativity and strong electrophilicity (569.13 kJ·mol⁻¹). OLFs(OH)⁻ was achieved by hydroxylating addition reaction when hydroxyl free radicals contacted with OLFs and attacked unsaturated double bonds with π electrons on surface of OLFs. And then anion radicals were obtained by the action of oxygen molecules, followed by the formation of OLFs(OH)_n. Possible formation mechanism of OLFs(OH)_n is shown in Figure 5.

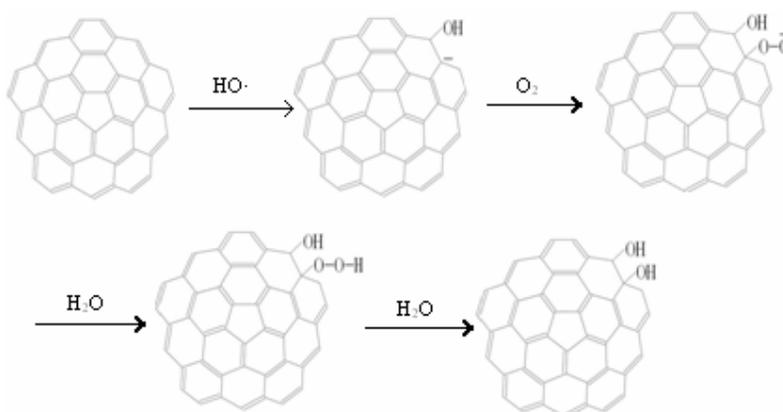


Figure 5. Possible formation mechanism of OLFs(OH)_n by reaction with melted KOH

Modification of OLFs by in-situ oxidation in radio frequency plasma

Figure 6 shows the HRTEM images of OLFs modified by radio frequency plasma. The products were metal-encapsulating OLFs with polyhedral or quasi-spherical morphology and uniform diameters of about 40 nm, as shown in Figure 6(a). Figure 6(b) is high-magnification image of OLFs. From Figure 6(b), it can be observed that OLFs with the diameter of 40 nm had low graphitization degree.

Figure 7 shows the FT-IR spectra of OLFs before and after modification in radio frequency plasma. As shown in Figure 7(a), only a peak at 1593 cm⁻¹ was clearly found on the surface of OLFs prepared only in Ar atmosphere. However, the bonds at 3430 cm⁻¹, 1783 cm⁻¹, 1624 cm⁻¹ and 1267 cm⁻¹, corresponding to stretching vibration of -OH, -COOH, -C=C- and C-O groups, respectively, were observed in Figure 7(b). This suggests that new oxygen-containing groups were introduced onto the surface of OLFs by radio frequency plasma using coal and ferrocene as raw materials in present of O₂ with the flow rate of 1.2 ml·min⁻¹.

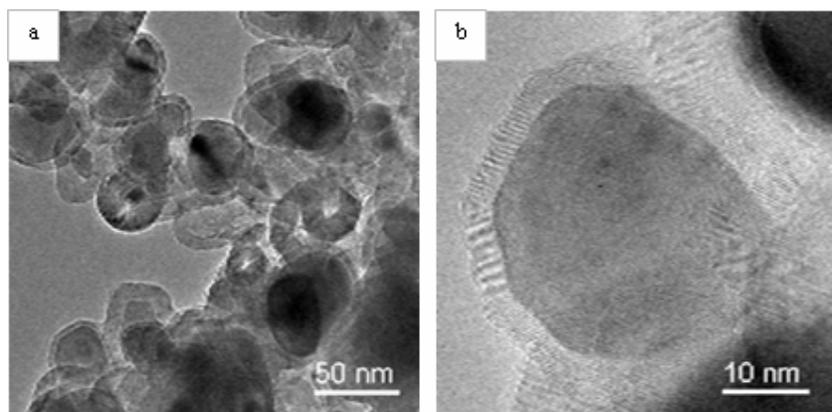


Figure 6. HRTEM images of OLFs modified by radio frequency plasma

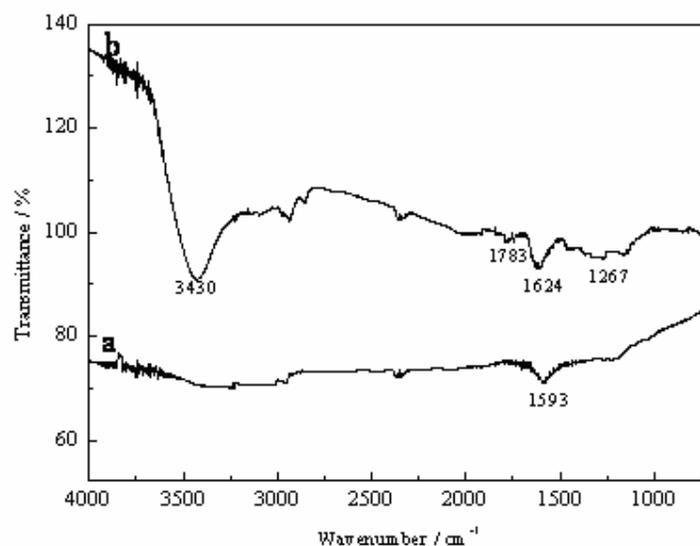


Figure 7. FT-IR spectra of OLFs treated in plasma with different content of oxygen: (a) 0, (b) 1.2ml/min

–OH and –COOH groups were formed on the surface of OLFs by oxidation of O₂ in plasma atmosphere to realize modification on OLFs in this experiment. After OLFs were prepared by decomposition of coal in Ar plasma, O₂ was introduced into plasma atmosphere to form hydroxyl free radicals on the surface of OLFs, followed by the formation of modified OLFs. The hydroxyl free radicals were converted into carboxyl groups when O₂ was continuously introduced into plasma atmosphere. However, the surface of the products was oxidized completely when the content of oxygen in atmosphere or the O₂-containing plasma treatment time were increased to a threshold value, resulting in change of the property of the products.

Conclusions

The raw OLFs were purified by reflux in nitric acid. HRTEM, TG and FT-IR measurement were used to analyze samples before and after purification. Results indicated that CNTs and OLFs were effectively separated; amorphous carbon and metal catalyst particles were removed by HNO₃ treatment and the purity of OLFs were improved. Moreover, the structures of OLFs were not influenced. This lays the foundation for further investigation of properties and applications.

Purified OLFs were chemically modified on surface through reflux with K in toluene and reaction with melted KOH. HRTEM and FT-IR characterization showed the formation of OLFs(OH)_n by these two methods. The structures of OLFs modified by toluene reflux were also affected. The diameters of OLFs modified by reaction with melted KOH became larger than those of purified OLFs.

Oxygen was introduced into plasma atmosphere after Huainan coal and ferrocene were reacted in Ar plasma for an hour so as to conduct in-situ modification on OLFs. The morphologies and structures of the products were characterized by HRTEM and FT-IR spectroscopy. The results revealed that –OH and –COOH groups were introduced onto the surface of OLFs by radio frequency plasma in present of O₂ with the flow rate of 1.2 ml·min⁻¹.

Acknowledgements

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