Component distribution of nano-carbon materials assisted by Time of Flight-Secondary Ion Mass Spectrometer

Ying Dong1,2, Fan Xu1, Yan Li3, Tinglu Song1* and Guoqiang Tan1,2*

1 Experimental Center of Advanced Materials School of Materials Science & Engineering, Beijing Institute of Technology, Beijing, 100081, China
2 Beijing Key Laboratory of Environmental Science and Engineering, School of Materials Science & Engineering, Beijing Institute of Technology, Beijing, 100081, China
3 Shenzhen Ori Technology Co., Ltd, Shenzhen, Guangdong, 518107, China
*Corresponding author’s e-mail: song@bit.edu.cn; tan123@bit.edu.cn

Abstract. Currently, there exist various materials surface analysis and characterization techniques, but it is difficult to measure their component distribution, in particular from a three-dimensional prospect. In this paper, the component distribution of nano-carbon materials in 2D and 3D views were both characterized via Time of Flight-Secondary Ion Mass Spectrometer (TOF-SIMS). The results indicate that TOF-SIMS could provide comprehensive information about component distribution, which is expected to be developed as an advanced technology in material analysis and characterization to the research community.

1. Introduction
The completion of materials analysis and characterization depends on advanced technologies[1]. In recent years, more advanced demands have been required for materials analysis and characterization, such as the detection limit, the spatial resolution and sensitivity, etc., which promotes the development of materials analysis and characterization technology. Among them, TOF-SIMS technology has attracted much attention and has been applied into various fields.

TOF-SIMS is a technology that combines time of flight (TOF) and secondary ion mass spectrometry (SIMS). The basic principle is to employ high energy primary ion sources (e.g., Ga+, Bi3+, etc.) to shine on the sample surface and excite secondary ions with the same initial kinetic energy. Ions that generated at the surface with different m/z values will then reach the detector at different times. The information about elements, isotopes, molecular structure and chemical bonding could be obtained. In addition, by using TOF-SIMS technology, not only the surface component information can be acquired, but also in the depth direction through continuous sputtering, which is illustrated in depth profiles, 2D and 3D images[2-4].

Nowadays, TOF-SIMS has been widely employed in various fields, such as semiconductor devices, nano devices, biomedicine, quantum structure, high-energy secondary batteries, high-tech materials including polymer materials, metals, semiconductors, glass ceramics, nano coating, paper, film, fiber, etc[5-7]. Compared with other surface analysis and characterization techniques, TOF-SIMS exhibits several advantages, such as a high spatial resolution of 70 nm, a ppb level detection limit, and excellent sensitivity. The main application capabilities of some popular surface analysis and characterization techniques were summarized in Table 1.
Table 1. Comparison of some popular surface analysis and characterization techniques in main application capabilities\[^8\].

|                     | XPS | AES | TOF-SIMS | SEM-EDS | XRF |
|---------------------|-----|-----|----------|---------|-----|
| Signal type         | electron | electron | secondary ion | X ray | X ray |
| Detection depth     | \(~ 10\) nm | \(~ 5\) nm | \(~ 1\) ~ 2 nm | \(~ 1\) μm | \(~ 2\) μm |
| Detectable element  | Li ~ U | Li ~ U | H ~ U | B ~ U | F ~ U |
| Detection limit     | 0.01% | 0.1% | ppb | 0.1% | ppm |
| Chemical analysis   | excellent | general | excellent | - | - |
| Depth profiling     | excellent | excellent | excellent | need to spray gold | excellent |
| Insulation materials| excellent | general | excellent | - | - |
| Spatial resolution  | 10 μm | 8 nm | 70 nm | 1 μm | 1 mm |

With the rapid development of nanomaterials, its surface analysis and characterization are particularly important. This paper aims to analyze and characterize nanomaterials assisted by TOF-SIMS, and obtain rich and comprehensive information about the component distribution, so as to show that TOF-SIMS could be considered as a simple, fast and efficient method for nanomaterials analysis and characterization. It’s necessary to introduce this technology because it could provide component distribution of nanomaterials from a 3D prospect, which could not be achieved via other technologies.

2. Materials and methods

Samples: Three samples were involved in this paper. The sample 1# was carbon paper produced by Toray Company of Japan. The sample 2# was carbon paper after cycling in a half cell with lithium metal. The 3# sample was obtained when the 2# sample used as the cathode material of the lithium-oxygen battery after discharging.

Equipment: ULVAC-PHI, Inc, Equipment type: PHI nano TOF II.

Each image had 512×512 pixels. TOF-SIMS depth profiling used 3 keV Ar\(^+\) ion sputtering with an area of 400um×400um. The beam current was approximately 100 nA.

3. Results and discussion

3.1. Images of surface component distribution

Figure 1. TOF-SIMS secondary ion images of sample 2# under negative (-) ions mode (the length of scale bar is 100 μm).
TOF-SIMS secondary ion images of sample 2# are shown in figure 1, which directly reflects the distribution of chemical species on the surface of the sample. The essential form of carbon fibers with sub-nano scales could be observed in these images. In addition, the chemical species on the surface of the sample grow uniformly attached to the carbon fibers. Among all, the intensity of O element is the highest\[9\].

Figure 2. TOF-SIMS secondary ion images of sample 3# under negative (-) ions of UB mode (the length of scale bar is 50 µm).

Figure 2 shows the distribution of several major chemical species (C, F, Li$_2$O$_2$) on the surface of sample 3#. The C and F elements grow along the carbon fibers, which exhibit a relatively high intensity. On the contrary, the discharging product of lithium-oxygen batteries, Li$_2$O$_2$, is usually hard to be probed via other surface analysis and characterization techniques. However, the existence of Li$_2$O$_2$ could be detected by conducting TOF-SIMS measurement, which further indicates its high sensitivity and low detection limit\[10\].

3.2. Mass spectrum

Figure 3. The mass spectrums of sample 3# by selecting two different areas derived from TOF-SIMS under negative (-) ions mode (the length of scale bar is 50 µm).

As can be observed from the left part of figure 3, the sample with different areas exhibit different light and dark degrees, which may be caused by disparate component intensity. To explore the reason, the mass spectrum of the region can be measured via TOF-SIMS to analyze the distribution and intensity of its components. The results indicate that the distribution of components in different regions are different. To be more specific, the brighter region contains more O and F elements, while more C element, C-H chemical bonding, C$_2$H and LiF components exist in the darker region\[11\].
3.3. Depth profiling

As is shown in figure 4, the 3D images obtained by TOF-SIMS show a relatively uniform distribution of C element within the material in all three samples, while the opposite trend is observed for most of other species. In sample 1#, the O element and C-H chemical bonding are evenly distributed. As for sample 2#, after cycling in the lithium-ion battery, it is found that the distribution of C-H chemical bonding and F element in the material are different from each other. The intensity of the former is high at both sides of the material, while the latter is high only at one side. The intensity of O element in sample 3# is higher than sample 2#, which may be attributed to the generation of oxygen-containing compounds LiOH and Li2O2 during the discharging behavior of lithium-oxygen battery. In addition, the spatial distribution of C-H chemical bonding also changes, which exhibits a reduced trend from surface to the bulk in terms of intensity. However, LiF is mainly distributed at one side of the sample, while Li and Li2O2 exhibit a relatively even distribution within the sample[12].

4. Conclusions

In summary, we have characterized the component distribution of three nanoscale samples assisted by TOF-SIMS and discussed about it from three aspects of 2D/3D images and mass spectrums. As an advanced technique, TOF-SIMS exhibits various merits including high detection limit, high spatial resolution, good sensitivity, etc. Moreover, TOF-SIMS has an incomparable advantage over other technologies, that is providing 3D images of material component distribution, which confirms the great necessity of this paper. In future studies, we hope to gain more information about the material at smaller nanoscale. A broader application of TOF-SIMS technique in nanomaterials is expected in the near future.

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