

SURFACE MODIFICATION OF GRAPHENE OXIDES

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Introduction

Crystalline carbon materials, including carbon nanotubes, graphene and their derivatives, have been in the focus of recent studies due to their unique structural, physical and chemical properties. They are promising candidates for a wide variety of applications, e.g. within the fields of energy storage and energy conversion, supercapacitors or catalysts supports in fuel cells, novel structural materials, field emission devices, pharmaceutical drug-delivery vectors as well as bio-sensing. Most of these functions require some form of surface modification, which explains the great effort that has recently been devoted to such investigations. The various applications of nanocarbon materials including graphene and graphene oxides often require surface modification, which explains the great effort that has recently been devoted to such investigations. Inclusion of heteroatoms is one of the most promising tools of tuning both the physical and chemical characteristics. The effect of various surface modification methods including mild thermal, chemical and radio frequency (RF) treatment are compared in this presentation.

Materials and Methods

The light brown graphene oxide (GO) suspension of 1 w/w% was obtained from natural graphite (Tyn, Spon.Sr.O, China; average particle size 0.063 mm, purity 95 %) by the improved Hummers' method¹. GO was freeze dried to obtain GOlio which was further treated i) in ambient air at 110 °C yielding sample GO110 and ii) at 300 °C in argon flow resulting the thermally reduced graphene oxide sample (TRGO). The chemically reduced GO (CRGO) was prepared from the aqueous suspension applying aqueous ascorbic acid (AA) in the presence of ammonia at 95 °C for 1 h². The sample was freeze-dried. Methods, including powder X-ray diffraction (XRD), infrared (FTIR-ATR) and Raman spectroscopy as well as Mass Spectrometry coupled thermogravimetric measurements (TG-MS) were applied for the characterisation of the initial samples.

Radio frequency (13.56 MHz) nitrogen plasma treatment was performed in the preparation chamber of the XPS instrument (base pressure <10⁻⁴ Pa). The high purity N₂ (5 N) flow of a few ml/min (STP) was regulated by a bleeding valve that set the pressure to 5 Pa. Constant power (100 W) was applied for 10 min. The treated samples were transferred to the analysis chamber without being exposed to the ambient air. Quantitative X-ray photoelectron spectroscopy (XPS) were employed to reveal the chemical differences of the initial and plasma treated samples.

Results and Discussion

Figure 1 compares the C1s region of the XPS spectra of the samples prior to the plasma treatment. The effect of the sample pre-history on its surface chemistry is shown in Figure 2. The assignment of the various species are listed in Table 1³. The changes in the corresponding C3 - O2, C4 - O3 - O1 - O2 and C5 - O1 states are consistent.

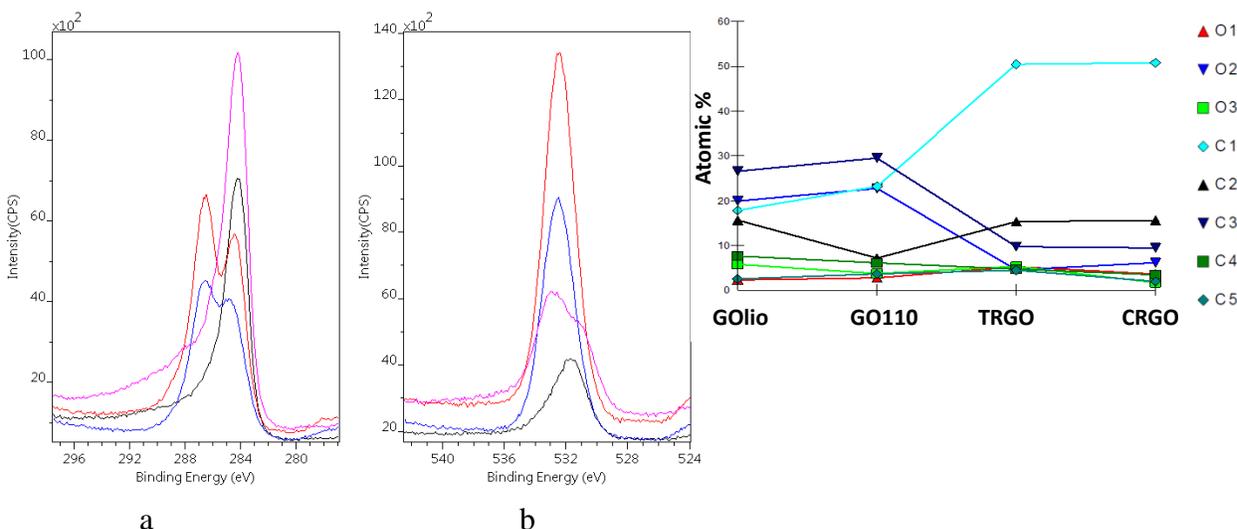


Figure 1 C1s (a) and O1s (b) regions of the initial graphene oxide samples. Color code: blue: GOlio; red: GO110; magenta: TRGO; black: CRGO

Figure 2 Distribution of the various C and O species in the precursor samples. See Table 1 for the various species³

Table 1 Identification of the C1s and O1s species in Figure 2³

Component	Assignment
O1	O in carbonyl group
O2	O in ether and epoxy, OH in alcohol, C=O in ester
O3	C-O-C in ester, OH in carboxyl
C0	sp ² C in graphite/graphene plane
C1	C-N bond in pyridine ring or amine, C in hydroxyl, ether or epoxy bond
C2	C-N bond in graphite plane, C in carbonyl bond
C3	C in amide bond, C in carboxyl or ester bond

The influence of the plasma treatment on the surface chemistry is illustrated in the CRGO sample (Figure 3).

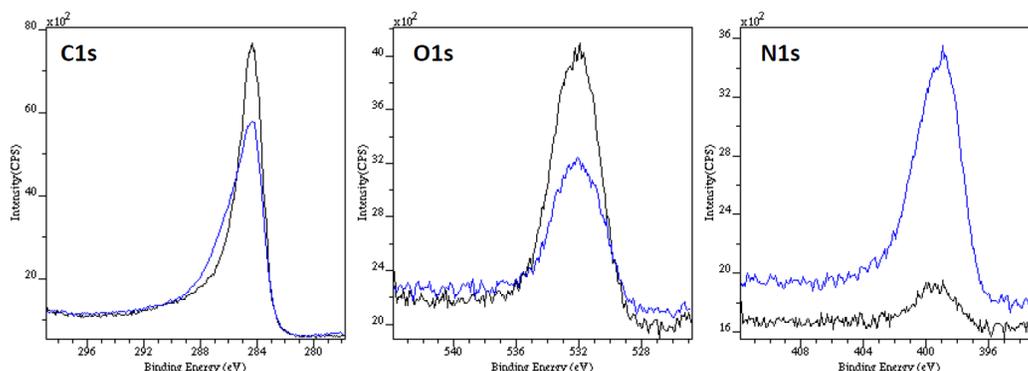


Figure 3 The C1s, O1s and N1s regions in the CRGO sample before (black) and after (blue) the plasma treatment

The treatment resulted in the inclusion of nitrogen heteroatoms, up to 2.6 atomic %. The shape of the N1s region as well as the widening of the C1s signal reveal that the nitrogen is incorporated in various chemical forms identified as sp² N in pyridine type ring, sp² N in pyrrole, diazine or triazine type ring structure and N substituting C in graphite plane.

Conclusions

Both the thermal and chemical reductions were able to modify the chemical composition of the GO derivatives. The extent of reduction can be tuned by the reaction conditions (temperature, concentration, time). It was also demonstrated that the surface of the GO derivatives can be conveniently modified using RF plasma activated low pressure nitrogen. The amount and nature of the nitrogen can be tuned by the duration of the treatment. These methods are simple ways to alter the surface composition and thus among other features, the hydrophobic/hydrophilic character of the carbon nanoparticles.

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