

EFFECT OF SURFACE MODIFICATION ON STRUCTURAL AND THERMAL PROPERTIES OF NANOCARBONS OF DIFFERENT DIMENSIONALITIES

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Abstract. Multi-walled carbon nanotubes and graphite nanoplatelets were functionalized *via* acid treatment to overcome the problem of agglomeration. Fourier transform infrared spectroscopy showed the chemical modification of the nanocarbons while the general relationship between the chemical treatment and the defects population was analyzed by Raman spectroscopy. The information regarding the mass loss and impurities is obtained from the thermogravimetric analysis. X-ray diffraction showed the effect of acid treatment on the physical states of the nanocarbons including the crystalline texture. The comparative high interlayer distance in graphite suggested that graphite particles are exfoliated into sheets of graphene by this technique with smaller particle sizes. The thermogravimetric analysis confirmed the complete removal of impurities in the case of multi-walled carbon nanotubes (MWCNTs) and about 20 % of impurities as seen in oxidized graphite attributable to the presence of residual manganese that might have been introduced during the functionalization process. Moreover, the thermal stability was also observed well in the case of MWCNTs with lesser impurities left. Overall, two different nanocarbons with well-structured chemical modifications were obtained with a variation in the feasibility of functionalization.

Keywords: nanocarbons, agglomeration, chemical modification, spectroscopy, defects

1. Introduction

Carbon-based conducting fillers such as carbon nanotubes and graphite nanoplatelets have been attracting worldwide attention because of their high aspect ratio, and superior electrical, thermal and mechanical properties.^{1–4} Owing to their superior properties, they have been used as filler in polymer composites proving a wide commercial application in the field of aerospace engineering, transportation, automotive and electronic industries.^{5–11} However, the problems with these materials stuck with the homogenous dispersion, *i.e.*, nanomaterials tend to agglomerate due to the intermolecular van der Waals interaction between the tubes and the graphitic layers or tubes which possess the major challenges, in the fabrication of nanomaterials composites.^{12,13} In addition to this, commercially available pristine multi-walled carbon nanotubes (MWCNTs) contain a mixture of the metal catalyst and amorphous carbon as well as impurities that can degrade the physical properties of nanocarbons.

Graphite exists as layered material and for its efficient utilization in polymer composites; the layer must be separated and dispersed. It is three-dimensional allotropes of carbon-containing carbon-carbon covalent networks and layers of graphene sheets that stack along with the *c*-axis due to the presence of van der Waals forces, and the separation of these layers is a considerable challenge.¹⁴

To overcome those challenges, nanocarbons can be chemically modified to enhance their overall properties with different kinds of organic molecules for better compatibility with the polymer matrix.¹⁵ Various methods are proposed for the surface modification of the MWCNTs such as covalent, non-covalent, π stacking and endohedral functionalization procedures. Among them, covalent functionalization has been widely used for the surface modification of carbon nanotubes (CNTs) which results in stable and stronger bonding. In addition to this, the surface modification of graphite nanoplatelets was carried out by liquid oxidization of nitric acid, sulfuric acid and a mixture of both.^{16–19}

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On acid oxidation, various oxygen-containing functional groups were found to be attached to the wall of these carbon-containing materials. Different types of acids and their mixtures such as HNO₃, HCl, and a mixture of HNO₃ and H₂SO₄ were used in the oxidation of CNTs.^{20–26}

Treatment with acid or a mixture of acids helps in the removal of metals and other impurities present in the CNTs which might have been introduced during the synthesis process. It further helps to overcome the hydrophobicity problem of CNTs and provides the condition for faster electron transfer causing increased conductivity.^{27,28} However, still, the effect of surface modification on properties of differently dimensional nanocarbons with complementary results from spectroscopic, thermal and microstructural analyses is yet to be explored. Hence, in this paper, the effect of surface modification of two different kinds of nanocarbons (namely one-dimensional multi-walled carbon nanotubes and two-dimensional graphite nanoplatelets) on their structural properties has been studied.

2. Experimental

2.1. Materials

Pristine multi-walled carbon nanotubes (MWCNTs, Nanocyl 7000) were purchased from Nanocyl SA and graphite nanoplatelets (Conductograph GFG50M) from SGL Carbon GmbH, Meitingen (Germany). Other chemicals like concentrated HNO₃, H₂SO₄, NaNO₃, KMnO₄, and H₂O₂ were purchased from Fisher Scientific, India.

2.2. Functionalization of Nanocarbons

Pristine MWCNTs are inert and hydrophobic and thus there is a need for the introduction of different functional groups on the CNT surface through an oxidation process to improve their hydrophilicity. Different oxidants have been used to oxidize CNT surfaces, such as *aqua regia*, concentrated nitric acid, concentrated hydrochloric acid, piranha mixture, ammonium hydroxide/hydrogen peroxide mixture, etc. Various oxygen functional groups (–COOH, –COO–, –OH, etc.) were introduced on the MWCNT surface after the acid treatment.²⁷ The presence of oxygen-containing functional groups facilitates the exfoliation of CNT bundles and increases the solubility in polar media.²⁹

0.2 g of pristine multi-walled carbon nanotubes was oxidized by refluxing in concentrated nitric acid. The mixture was first sonicated and refluxed and filtered through a 0.2 μm polycarbonate membrane and washed with distilled water until pH 7 was obtained. The resulting product was dried in hot air at 373 K in the oven till it

dried.³⁰ Likewise, 0.2 g graphite powder was functionalized following the conventional Hummers method treating with conc. H₂SO₄ along with NaNO₃ and KMnO₄. This mixture was magnetically stirred for about half an hour at 308 K. The slurry was diluted with deionized water with the addition of H₂O₂ changing the blackish colour into yellow. Finally, the residues were washed, filtered and dried in hot air at 323 K in the oven till they dried.³¹

2.3. Techniques

Fourier transform infrared (FTIR) spectra were recorded by a Perkin Elmer FTIR 2000 Spectrophotometer operated in ATR mode over wavenumber range from 4000 cm⁻¹ to 400 cm⁻¹ with a resolution of 20 cm⁻¹. For every sample location, 20 scans were made.

Raman spectra were used to extract more information on structural variations caused by acid treatments and were recorded by Bruker SENTERRA I Raman microscope within the wavenumber ranges from 2000 cm⁻¹ to 400 cm⁻¹ with the excitation wavelength of 532 nm.

X-ray diffraction (XRD) of the samples was carried out in the powdered form by Rigaku D/MAX-2500/pc. The radiation source used was Cu Kα with a wavelength of 0.15406 nm. The specimens were scanned over the diffraction angle of 2θ range between 5° and 80°.

Thermogravimetric analysis (TGA). Thermal properties were studied by TGA Mettler Toledo TGA/SDTA 851 equipment under an oxygen environment over a temperature range from 303 K to 1273 K at the rate of 10 K/min.

3. Results and Discussion

3.1. Fourier Transform Infrared Spectroscopic (FTIR) Studies

FTIR is mainly used in the chemical identification and evaluation of functional groups present in substances. FTIR spectra of pristine and oxidized MWCNTs are shown in Figs. 1 and 2.

The spectrum of pristine MWCNTs did not show any sharp infrared peaks, indicating that it did not contain any functional groups on comparing the infrared spectrum of the oxidized MWCNTs to that of pristine one. Due to the acid treatment of pristine MWCNTs, several oxygen-containing functional groups were introduced. The appearance of a peak at 1700 cm⁻¹ is due to the C=O stretching of the carboxyl group, while the transmittance bands at 1306 cm⁻¹ and 1150 cm⁻¹ are associated with OH bending and C–O stretching, respectively. The integrity of hexagonal structure on MWCNTs was confirmed by the

appearance of a peak at 1600 cm^{-1} which showed the existence of carbon-carbon double bonding.³² The peak around 2900 cm^{-1} indicated the C-H asymmetric and

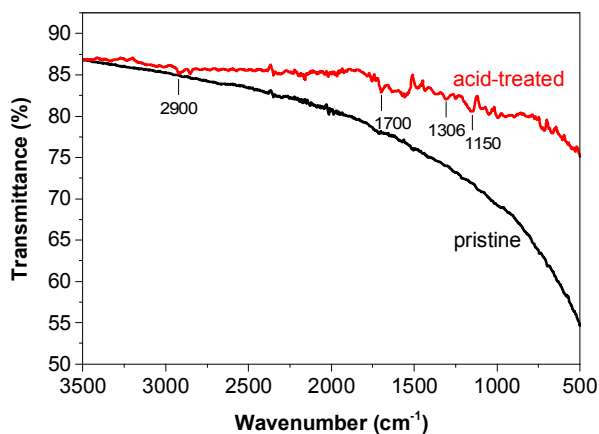


Fig. 1. FTIR spectra of pristine and acid-treated MWCNTs sample

Similar FTIR spectra were obtained on neat and modified graphite samples. The results are shown in Fig. 2. On acid oxidation of graphite powder, the slightly broad signal appears at around 3600 cm^{-1} which is due to the hydroxyl group suggesting that there are -OH functional groups on the graphite surfaces.³⁵ Along with this observation, the peak signal at around 1616 cm^{-1} suggests that there is -C=C stretching from the pristine graphitic domain.^{36,37}

The acid treatment was found to be successful in both pristine MWCNTs and pristine graphite. Likewise, OH stretching vibration of the hydroxyl group was commonly seen in the case of both the treated samples whereas the carbonyl group distinctly appeared in the case of MWCNTs only. Also, other various groups were observed indicating an effective acid treatment and some pristine graphitic domain persists in graphite nanoplatelets sample.³⁶

The first method in the absence of refluxing was also used to functionalize nano-diamond which yields good results (unpublished results). Finally, it can be concluded that the method used in this study was effective in functionalizing the nanocarbons of different dimensionalities.

3.2. Raman Spectroscopic Investigation

The results of Raman spectroscopy are summarized in Figs. 3 and 4. In the case of MWCNTs, the two intense peaks corresponding to D and G bands were prominently seen in Raman spectra. The D band is due to the presence of structural defects (that means the defects due to the generation of amorphous carbon produced during oxi-

symmetric stretching vibrations of the long-chain nature of the alkyl group.^{32,33} Furthermore, the O-H stretching vibration of the hydroxyl group was seen at 3200 cm^{-1} .³⁴

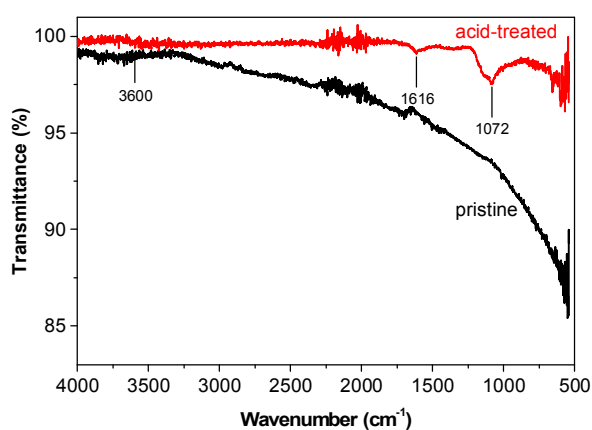


Fig. 2. FTIR spectra of pristine and acid-treated graphite sample

dation and conversion of sp^2 carbon to sp^3 carbon) in the nanocarbon whereas the G band occurs due to the tangential stretching of the carbon-carbon bonds. The D band occurs due to the presence of amorphous or disordered carbon in the MWCNTs because of its nanosized structure). The D and G bands in pristine and treated MWCTs were seen at 1334 cm^{-1} and 1572.5 cm^{-1} as well as 1341.5 cm^{-1} , and 1581.5 cm^{-1} , respectively. It has been suggested that the intensity ratio of the D band (I_D) and the G band (I_G), I_D/I_G , determines the degree of disorder, sp^2 domain sizes³⁸ and presence of the defects in the nanocarbons. Indeed, the value of I_D/I_G , for pristine MWCNTs was found to be 1.13 whereas for functionalized MWCNTs was 1.22. In this way, the magnitude of the ratio I_D/I_G can be used to evaluate the defect density of the multi-walled carbon nanotube.^{39,40}

Similarly, the intense peaks at 1342 cm^{-1} and 1572 cm^{-1} as well as 1341.5 cm^{-1} and 1573 cm^{-1} , respectively, in Fig. 4 correspond to the D and G bands which are typical for nano-graphitic materials before and after oxidation. The value of I_D/I_G was found to be 0.22 and 0.24 for the pure and the functionalized graphite powder, respectively.^{41,42} It indicates the increase in defect sites on the surface of graphite samples. These defect sites may be amorphous carbon generated as a result of oxidation and conversion of sp^2 carbon to sp^3 carbon.

In both nanocarbons, the position of the D and G bands are shifted towards the higher wavelength which may be due to the doping effect upon acid treatment. The presence of these two characteristics peaks after oxidation suggested that there is no damage to the graphitic integrity of nanocarbons.⁴³

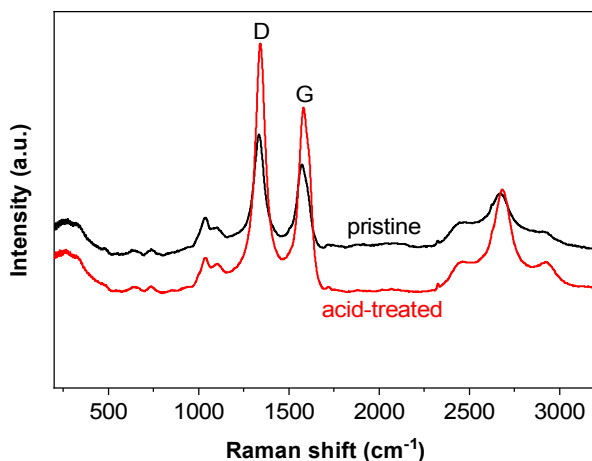


Fig. 3. Raman spectra of pristine and acid-treated MWCNTs sample

Similar results were also reported in the previous work.⁴⁴ The increase in the magnitude of I_D/I_G value suggests that the structural defect occurs by the transformation of sp^2 structure (that is representative of a graphite-like structure) to the sp^3 (diamond-like structure).

Hence, from the above intensity ratio, multi-walled carbon nanotubes were found to be more susceptible to functionalization with acids. This might be due to the grafting of $-COOH$ groups on multi-walled carbon nanotubes with HNO_3 oxidation and the absence of $-COOH$ functional groups in the functionalized graphite.

3.3. X-Ray Diffraction (XRD)

Additionally, the structural properties of the nanocarbons were studied by X-ray wide-angle diffraction technique as shown in Figs. 5 and 6.

In the X-ray diffractogram, the average particle size D was calculated using the Scherrer equation

$$D = 0.9 \lambda / (\beta \cos \theta) \quad (1)$$

where λ is the wavelength of the X-ray used (0.154 nm) and β is the full-width half maxima of the peak in radians. The interlayer spacing d_{002} between the planes is calculated by the equation

$$d_{002} = n\lambda / (2 \sin \theta) \quad (2)$$

The Bragg peak (002) was observed at 25.92 and 25.68 degrees for pristine MWCNTs and acid-treated MWCNTs, respectively. After oxidation of pristine MWCNTs, the d -spacing value was found to be increased indicating the removal of carbon impurities present between the layers.⁴⁵

In the case of graphite nanoplatelets, the Bragg peak corresponding to the (002) plane was observed at 26.33 degrees for pure corresponding to a d -spacing of

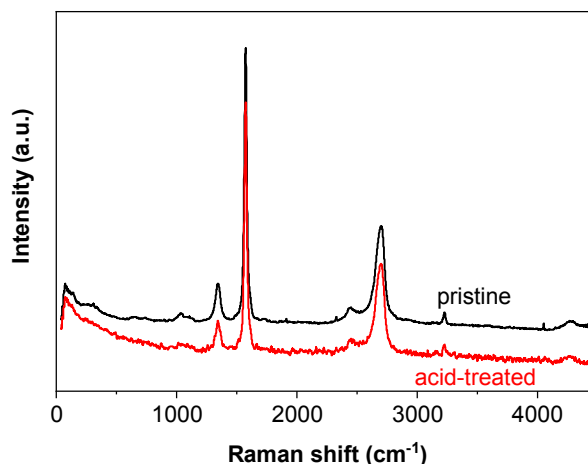


Fig. 4. Raman spectra of pristine and acid-treated graphite nanoplatelets sample

0.301 nm in the XRD pattern of the graphite sample. On oxidation of pure graphite, the (002) peak shifted to a lower angle at 10.14 degrees (d -spacing: 0.783 nm). This increase in d -spacing is due to the interaction of water molecules and the generation of oxygen functionality in the interlayer spacing of graphite which is in agreement with the above-presented result.⁴⁶ There was not much change in particle size of MWCNTs before and after functionalization but in the case of graphite, the particle size decreased from 17 nm to 3 nm. This was because the oxidizing agents partially broke the graphite nanoplatelets into smaller particles indicating that it has been subjected to the highest degree of molecular distortion in graphite.⁴⁷ The (002) broad peak was observed for acid-treated graphite than the pure sample which implies that the degree of crystallinity deteriorated after the acid treatment process further confirmed by calculation.

The size of the particles along with interlayer distance drastically varies in the case of graphite on comparing with MWCNTs. The degree of crystallinity is also found to deteriorate after the acid treatment in the case of graphite (16.4 % to 15.5 %) whereas the opposite trend was found in the case of MWCNTs (20.3 % to 29.2 %).

3.4. Thermogravimetric Analysis (TGA)

Fig. 7 shows the TGA thermograms of pristine and oxidized MWCNTs. In the case of pristine MWCNTs, drastic weight loss occurred (approximately 80 %) at temperatures ranging from 823 to 923 K. This reveals that all MCNTs were burned out at this temperature range and the weight remained constant up to 1273 K. The residue left (about 20 %) corresponds to the weight expected for some of the oxidized metals present as impurities.⁴⁸

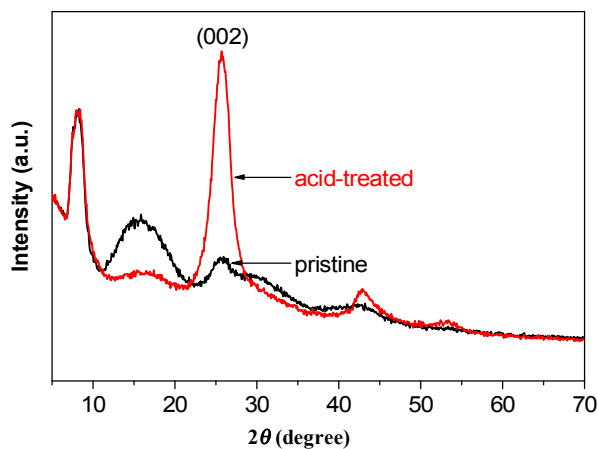


Fig. 5. XRD spectra of pristine and acid-treated MWCNTs samples

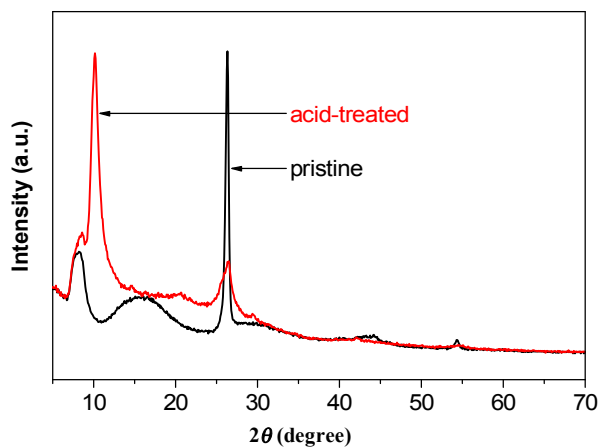


Fig. 6. XRD pattern of pristine and acid-treated graphite sample

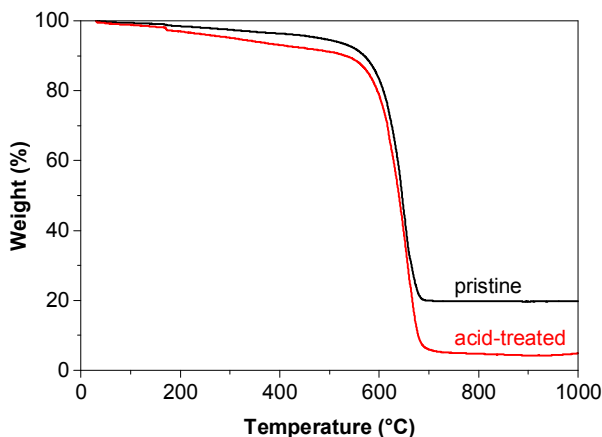


Fig. 7. TGA curves of pristine and acid-treated MWCNTs samples

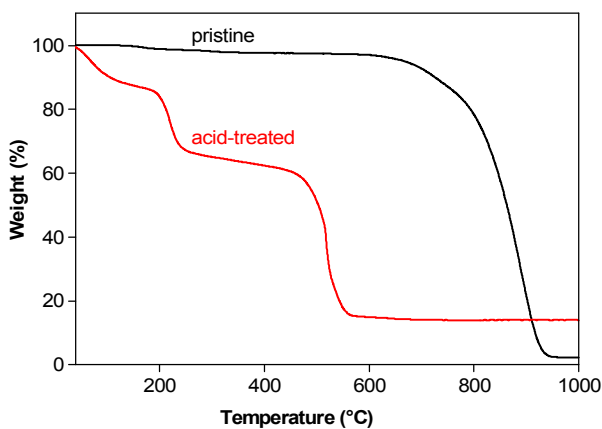


Fig. 8. TGA curves of pristine and acid-treated graphite sample, showing stepwise degradation of modified graphite samples

However, in the case of the oxidized MWCNTs, the weight loss on heating the sample from 373 K to 473 K was due to the loss of water molecules because oxidized MWCNTs are hydrophilic. At around 473 K – 623 K, some weight loss was seen in the TGA curve. The weight loss may be due to the loss of some amorphous carbon, which was generated during the oxidation and decomposition of different functional groups formed after the acid treatment. This confirmed the introduction of oxygen functional groups after acid treatment.⁴⁹ The significant weight loss occurred at around 823–923 K indicating the combustion of all MWCNTs. The lower weight percentage on comparing with the pristine (about 3 %) is definite evidence of the removal of the metal impurities after acid treatment.

Hence, the metal impurities present in the pristine MWCNTs are removed while after acid treatment oxidized graphite loose different moisture, hydroxyl groups, and

amorphous carbon on thermal degradation. Pure graphite has no weight loss until 923 K. However, the acid-treated graphite powder has a reduction in van der Waals interactions compared to pure graphite powder and hence lower thermal stability was observed. The noticeable stepwise thermal degradation in oxidized graphite suggested the removal of water molecules, hydrogen atoms and hydroxyl groups showing successful functionalization.⁵⁰ However, the trace of impurities of about 20 % was seen in the oxidized graphite due to the considerable amounts of residual manganese because of the use of permanganate oxidant⁵¹ graphite compared with pure graphite which might be due to the removal of water molecules, the hydrogen atom. The stepwise removal of impurities hence was observed clearly in the thermogram in the case of acid-treated and hydroxyl groups added after the oxidation.

In summary on studying the thermograms of both acid-treated MWCNTs and graphite, MWCNTs show

normal weight loss behaviour over the stepwise weight loss of graphite. Along with this the residual after acid treatment can be seen higher in the case of graphite which might be due to the use of the permanganate oxidant during functionalization.

4. Concussions

1. FTIR shows the attachment of different functional groups on its surface. A higher number of functional groups were found attached with MWCNTs rather than in the case of the graphite sample.

2. Surface modification of carbon-containing materials with oxygen-containing functional groups was obtained by treating MWCNTs with conc. HNO₃ and graphite sample with conc. H₂SO₄. Oxidation with acid increases the defect population confirmed by Raman spectroscopy. The Raman study concluded more numbers of defective sites with the MWCNTs.

3. XRD spectra further supported the interpretation of the surface modification of nanocarbons on acid treatment. The comparative high interlayer distance in MWCNTs suggested that graphite particles are exfoliated into sheets of graphene by this technique with smaller particle sizes.

4. TGA confirmed the complete removal of impurities in the case of MWCNTs and about 20 % of impurities as seen in oxidized graphite due to the manganese. Moreover, the thermal stability was also observed well in the case of MWCNTs with less impurity left.

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ВПЛИВ МОДИФІКАЦІЇ ПОВЕРХНІ НА СТРУКТУРНІ ТА ТЕРМІЧНІ ВЛАСТИВОСТІ НАНОВУГЛЕЦІВ РІЗНОЇ РОЗМІРНОСТІ

Анотація. Багатошарові вуглецеві нанотрубки та графітові нанопластинки були функціоналізовані через обробку кислотою з метою подолання проблеми агломерації. За допомогою інфрачервоної спектроскопії з перетворенням Фур'є

показано хімічну модифікацію нановуглеців, а загальний зв'язок між хімічною обробкою та популяцією дефектів проаналізовано Раман-спектроскопією. Інформацію про втрату маси та домішки отримано термогравіметричним аналізом. Рентгенівська дифракція показала вплив обробки кислотою на фізичні стани нановуглеців, у тому числі на кристалічну текстуру. Порівняно висока міжшарова відстань у графіті свідчить про те, що за допомогою цієї методики частинки графіту розширюються на листи графену з меншими розмірами частинок. Термогравіметричний аналіз підтвердив повне видалення домішок у випадку багатошарових вуглецевих нанотрубок (БШВНТ) і близько 20% домішок в окисленому графіті, що пояснюється наявністю залишкового марганцю, який міг бути введений під час процесу функціоналізації. Крім того, також спостерігали хорошу термічну стабільність у випадку БШВНТ з меншою кількістю домішок. Загалом було отримано два різних нановуглеці з добре структурованими хімічними модифікаціями з різними можливостями функціоналізації.

Ключові слова: нановуглеці, агломерація, хімічна модифікація, спектроскопія, дефекти.