ENVIRONMENTALLY FRIENDLY APPROACHES FOR CHEMICAL MODIFICATION OF CARBON-BASED NANOMATERIALS

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Abstract

Carbon-based nanomaterials are under investigation for different applications, which often demands their chemical modification such as introducing the amino-functional groups or removing carboxyl and hydroxyl groups. In this paper, we are presenting approaches for changing the structure of selected carbon-based nanomaterials in which the use of reactive toxic chemicals is avoided. The methods such as gamma irradiation, thermal treatment with a source of N atoms and nascent hydrogen reduction are studied as possible methods for modification of carbon-based nanomaterials. In the phase of the cleaning, again environmentally friendly approaches are used: filtration, centrifugation, and dialysis. Due to selected methods for both modification and cleaning, the presented approaches are environmentally friendly, they avoiding the use of both aggressive toxic chemical in the synthetic phases as well as organic solvents in the phase of cleaning. Thanks to the avoiding of dangers chemical, these methods can lead to the lowering of the waste chemicals producing in the long-term future.

Introduction

Carbon-based nanomaterials are attracting great scientific attention since they were discovered.[1] Fullerenes are first discovered carbon-based nanomaterial, than carbon nanotubes, followed by graphene, graphene, and carbon quantum dots. All these materials possess unusual chemical, electrical and biological properties which made them interesting for application in therapy of carcinoma, bioimaging, solar cells, etc.[2-5]

Due to the need for carbon nanomaterials with different polarity and solubility, chemical structures as well as electrical conductivity, a large number of chemical reactions were applied to these materials in order to achieve these demands.[6-8] These reactions often involve the use of highly reactive, explosive and aggressive chemical, while the phase of cleaning is based to use of large volumes of different organic solvents such as 1,2-dichlorobenzene, methanol, and others. After reactions are done, the large amounts of residual, waste chemicals are left to be properly handled. Considering their high toxicity to humans and the environment, appropriate managing of this waste is necessary. Considering the increasing number of carbon nanomaterials application, the need for green approaches with reduced use of toxic chemicals for their modification also increasing.

Thus, we proposed a few approaches for modification of carbon nanomaterials using eco-friendly approaches. As a model system, we used graphene quantum dots and graphene oxide. We applied gamma irradiation on this material, using only water and a small amount of isopropanol as a medium in order to achieved chemical reduction. This chemical modification is often achieving using hydrazine, cancerogenic chemical. Also, thermal treatment with urea in order to incorporate N atoms in GQDs is based only on the application of GQDs and urea,

as well as the heat. As an alternative to hydrazine reaction, we investigated the possibility of use of nascent hydrogen reduction. We investigated the effects of proposed reaction on the morphology and chemical composition of GQDs and GO.

Experimental

Synthesis of carbon-based nanomaterials was achieved using electrochemical approach and modified Hummer's method for GQDs and GO production, respectively. Electrochemical synthesis of GQDs involves the use of graphite rods as both cathode and anode and 3% dispersion of NaOH in ethanol (96%) as an electrolyte. The current was set to 20 mA. Next day (in 24 h), the electrolyte was change color from yellowish to dark brown. It was collected and neutralized with HCl. Formed flocculated NaCl was removed by filtration and dialyze against MiliQ water (molecular weight cutoff 3500 Da) for 3 days to remove the residual NaCl. Graphene oxide was produced using a modified Hummer's method. Graphite powder (1 g) was dispersed in concentrated H_2SO_4 (23.3 ml). Then $KMnO_4$ (3 g) was slowly added to the reaction mixture placed in the ice bath. Next, after 1h the temperature was increased to 40 °C for 30 min and to 95 °C for 15 min. After that, the reaction mixture was poured into water (200 mL) and filtrated until the pH was 7.

Chemical modification of GQDs and GO were achieved using different approaches. Reduction of GO was conducted using *in situ* generated hydrogen. GO or GQDs were dispersed in water in a concentration of 1 mg/ml and the HCl acid (35%) was added in the final concentration of 1 mol/l. The pieces of Al foil were added in a concentration of 4 mg/ml. The final products were isolated using dialysis named GO-H and GQDs-H. In order to modify their structure, we used gamma irradiation, in a dose of 50 kGy and the medium for irradiation mixture of MiliQ water with isopropyl alcohol. This sample is named GQDs-50. To incorporate N atoms in GQDs, 50 mg GQDs and 1 g of urea was mixed and placed in a flask and heated for 5 minutes, with a heat gun. Then the mixture was diluted in water and filtered, followed by washing with water and methanol to remove free urea. This sample is named GQDs-U.

Atomic Force Microscopy (AFM) measurements were performed using Quesant microscope (Agoura Hills, CA). The microscope was working in the tapping mode, at room temperature, and in the air. Mica was used as a substrate. Samples were deposited using spin-coating. Absorption measurements were performed at UV-Visible UV-2600 Spectrophotometer (Shimadzu Corporation, Tokyo, Japan) in the ranges of wavelengths from 200 to 800 nm with 1 nm step. Spectra are recorded at 20 °C, in the air environment. Samples were prepared in the form of water dispersion, at a concentration of 0.25 mg/ml. The elemental composition of the samples was investigated by scanning electron microscopy (SEM, JEOL JSM-6390LV) with energy dispersive spectrometry (EDS, Oxford Aztec X-max), operating in vacuum at room temperature and an acceleration voltage of 3 keV.

Results and discussion

The results of AFM measurements are presented in Figure 1. AFM images of GQDs are presented on the left side while accompanied height profiles are presented in the upper left corner in the each AFM images. The right side, next to each AFM image, both height and diameter distributions are presented. These results showed that p-GQDs are mostly 15 to 20 nm in the height while an average diameter is in the range between 5 and 10 nm. For GQDs-H, the lower hight was observed, between 10 and 15 nm, and the diameter is around 6 nm. For GQDs-U, the largest fraction of dots is 3 nm in the height and an average diameter in the range between 5 and 10 nm. In the case of GQDs-50, the largest fraction is a 7 nm in height and 5 to 10 nm in diameter.

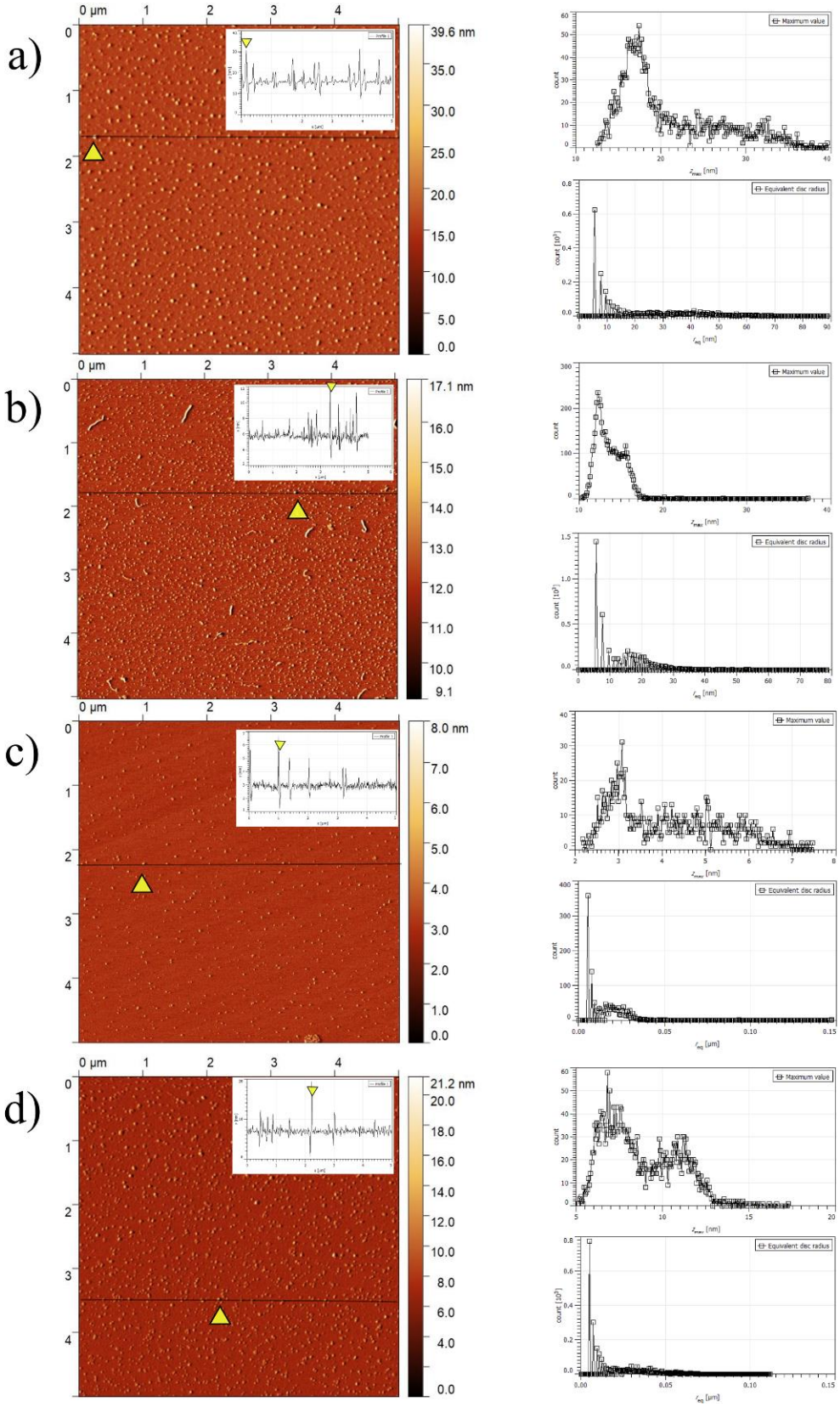

Figure 1. AFM images, profiles, height and diameter distributions for p-GQDs (a) and modified GQDs: GQDs-H (b), GQDs-U (c) and GQDs-50 (d).

The lowering in the height of GQDs after functionalization indicate reducing the number of functional groups.

The morphology of samples was also investigated using SEM microscope and while the EDS was employed to study the chemical composition of samples. In figure 2a), the SEM image of GQDs-50 has presented as well as the maps of O, Si, C atoms. It can be observed that sample contains 8% of O atoms, which is higher compared to GQDs-H (2%) [9] but significantly lower in comparison with p-GQDs, which has 37 % of O atoms.[10] These results indicate the lowering in the content of O containing functional groups.

UV-Vis spectra of all samples are present in figure 2b. The main absorption band for GQDs is located at 213 nm and it stems from π-π* transitions due to the presence of graphene core. The additional band can be observed at around 320 nm and it stems from carboxy functional groups. Due to modification, the main absorption band has been shifted to the higher wavelengths. This change can be assigned to increasing of π-domains in GQD and GO structure.

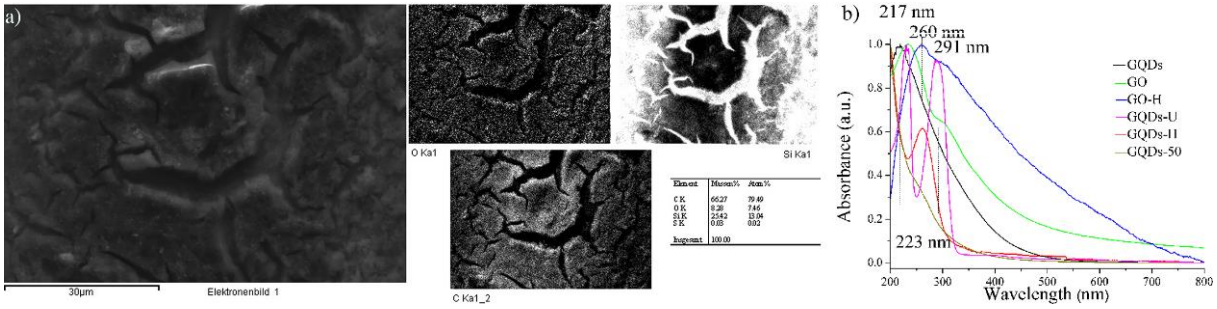

Figure 2. a) SEM image of GQDs-50 sample and elemental mapping, b) UV-Vis spectra of p-GQDs, GO, GO-H, GQDs-U, GQDs-H and GQDs-50 as indicated in spectra.

Conclusion

Proposed methods for structural modification of GQDs and GO appear to be efficient, eco-friendly methods for structural modification of carbon-based nanomaterials. By employing proposed reactions, the production of waste, residual, toxic reagents and solvents are avoided, while at the same time we achieved the chemical reduction of GO and GQDs. This structural modification is important from the aspect of the electronic application of these nanomaterials.

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