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Reduction of graphene oxide and graphene quantum dots using nascent hydrogen: The investigation of morphological and structural changes

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ABSTRACT

In order to modify both chemical and electrical properties of graphene-based nanomaterials, we conducted the chemical modification of graphene oxide (GO) and graphene quantum dots (GQDs). The reaction of the reduction with nascent hydrogen was conducted on both materials. The structure and morphology of produced chemically reduced GO and GQDs were analyzed. While the chemical composition of both GQD and GO changed significantly, GO showed also significant changes in morphology as opposite to GQDs where morphological changes were not observed.

KEYWORDS

graphene oxide, graphene quantum dots, chemical reduction, SEM-SMM-AFM

INTRODUCTION

Graphene is a carbon-based nanomaterial build solely of sp^2 C atoms organized in a hexagonal crystalline structure. To obtain graphene, different approaches have been employed in the last years [1]. In colloidal form graphene was produced by oxidation of graphite in order to obtain graphene oxide (GO) which is in the next step reduced using different methods [2]. The common methods for GO reduction are chemical reactions with hydrazine, hydroquinone, sodium borohydride, or dimethylhydrazine [2], or with solvothermal method [3], freeze-dried [4], etc. These chemicals are highly cancerogenic or explosive and furthermore they lead to the production of graphene with low electrical conductivity due to the introduction of additional functional groups. In this paper we generate a powerful reducing agent, nascent hydrogen (H^* or H – atomic hydrogen) directly in the reaction mixture using kitchen Al foil and HCl. This approach is eco-friendly, short-time and low price procedure. Thus, the procedure is suitable for the large scale production of reduced GO.

Additionally, we used the same procedure to modify the structure of graphene quantum dots (GQDs). GQDs are the youngest member of the graphene family [5]. With size below 100 nm, graphene core and a large number of oxygen-containing functional groups, GQDs can be considered as very small GO. By employing the described procedure, we aimed to remove oxygen functional groups from GQDs and investigate the effects of this procedure on GQDs morphology.

EXPERIMENTAL

For the synthesis of GQDs we used the previously applied electrochemical approach which includes the use of graphite rods as anode and cathode [6]. We dispersed 3 g of NaOH in 100 mL of ethanol (96 vol%) and used it as an electrolyte. Two graphite electrodes were connected to the current source and immersed in an electrolyte. As a source we used 224 Keithley Current Source. The applied current was set to 20 mA. After 24 h, the electrolyte was collected and used for isolation of GQDs: a) neutralized with HCl, b) filtrated to remove the flocculated NaCl and c) dialyzed (molecular weight cutoff 3,500 Da) for 3 days to eliminate the residual NaCl.

GO was synthesized using a modified Hummer's method. Graphite powder (1 g) was sonicated in cH_2SO_4 (23.3 mL) and placed on the ice bath. Then KMnO_4 (3 g) was slowly added to the reaction mixture and after 1 h 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 reduction of both GO and GQDs was conducted using *in situ* generated hydrogen [7]. Synthesized GQD and GO were dispersed in water in a concentration of 1 mg/mL and the cHCl acid (35%) was added to obtain the concentration of 1 mol/L. Then, Al foil was added to a concentration of 4 mg/mL. The releasing of the gas (H^*) was optically observed and after 3 h of bubbling, the gas formation was no more noticeable which indicated the end of the reaction. The final products were isolated using dialysis and named GQDs-H and GO-H.

Atomic Force Microscopy (AFM) measurements were performed using Quesant (Agoura Hills, CA) microscope

operating in tapping mode in the air, at room temperature. Samples were spin-coated on mica substrate. The morphology of the sample was investigated by Scanning Electron Microscopy (SEM, Hitachi S3200N SEM) in vacuum at room temperature, with an acceleration voltage of 3 keV. SEM Zeiss LEO 1450 and AFM and scanning microwave microscope (SMM) inside SEM chamber were used to investigate the structural and electronic properties of GO-H [8]. The elemental composition of samples was analyzed with Energy Dispersive Spectrometry (EDS), Oxford INCA EDX system with 10 mm² SDD detector, PentaFET Precision INCA X-act, 125 eV resolution, which detects elements from Be to Pu). Absorption measurements were performed at UV–visible UV-2600 Spectrophotometer (Shimadzu Corporation, Tokyo, Japan) from 200 to 800 nm, with 1 nm step. Water dispersions, the concentration of 0.25 mg/mL are recorded at 20 °C, in the air.

RESULTS AND DISCUSSION

In Fig. 1, the reaction scheme as well as photography of reaction mixture before and after the reaction is presented. The standard reduction potential of Al in acidic solutions is −1.66 eV which leads to fast dissolving of Al in the HCl and consequently to fast chemical reaction (just 3 h).

AFM analysis of GQDs showed that the height of non-modified GQDs is up to 21 nm, in the case of GQDs-H the highest GQDs are around 3 nm (Fig. 2a and b). This result indicates the lowering in GQDs height which is often associated with the lowering of the amount of oxygen-containing functional groups. The analysis of the chemical composition of GQDs-H (Fig. 2c) shows that O is present

Fig. 1. Reaction scheme and photography of reaction mixture before and during the reaction (after 1 h)

Fig. 2. AFM images of non-modified GQDs (a) and GQDs-H (b). SEM EDS maps for C and O, for GQDs-H (c)

in a low percentage in the GQD structure (only 2.78% mass). This is significantly lower compared to our results recorded for non-modified GQDs (35.3%) [9]. These results suggest that GQDs-H has been successfully produced and that selected cleaning procedure was highly efficient considering that none of the used reagents was detected in the final product. Also, the Al nanoparticles did not adhere to the surface of GQDs as some study suggested in the case of GO.

On the other hand, proposed chemical reduction of GO caused the changes in the morphology of graphene sheets: flat sheets with one to three layers of graphene after reduction became wrinkled and folded (Fig. 2a and b). The average height of GO-H sheets is around 1 nm which indicates that GO-H is a mostly single layer, and it is lower than an average height measured for GO (1.5 nm). UV-vis spectrum of GO-H (Fig. 3e) shows the red-shift of the band from 234 (as observed for GO) to 262 nm. This band stems from $\pi \rightarrow \pi^*$ transitions of aromatic C–C bonds. The band at 300 nm can be clearly observed in the spectrum of GQDs and it is assigned to $n \rightarrow \pi^*$ of carbonyl groups. This band cannot be observed in the spectrum of GO-H. These results suggest that the conjugated region was increased and that the content of carbonyl groups is reduced.

To investigate both morphology and electrical properties of GO-H, multimodal imaging technology, SEM-SMM-AFM was used (Fig. 4.). These analyses showed flat morphology of GO sheet (Fig. 4a), but Fig. 4b and c were obtained by inducing microwave energy into a Platinum-AFM-Cantilever probe of 50 nm radius. The two latter images exhibits strong contrast of 1.5 dB or 5 deg respectively, and reveals structures of conductive areas at 3.9 GHz, not visible in the AFM image.

CONCLUSIONS

Presented results lead to the conclusion that both GQDs and GO have been successfully chemically reduced using *in situ* generation of nascent hydrogen due to the lowering of oxygen content from 35.3 to 2.78%. Produced materials lost the bands at 300 nm in UV-vis spectra indicating the lower amount of carbonyl functional groups. We observed electrical conductivity of the whole graphene sheets including the edges, which additionally proves chemical reduction. Thus in future work we will use these materials to produced thin films and investigate their activity as shields for microwave irradiation.

Fig. 3. AFM images of GO (a) and height profile (b), GO-H (c) and height profile measured at positions indicated with blue lines (d). UV-vis spectra of GO and GO-H, as indicated on curves (e).

Fig. 4. SEM-SMM-AFM images of GO-H: AFM (a), Complex reflection coefficient S_{11} image of GO, mag (S_{11}) (b) and phase shift arg (S_{11}) (c).

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